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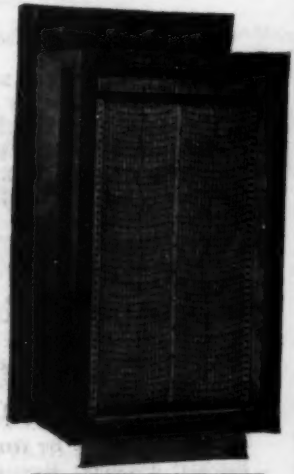

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CONTENTS.

	PAGE
Council and Officers	i–ii
Committees	ii–iv
General Notices :—	
Copyright	vi
Issue of Journal	vi
Changes of Address	vi
Papers and Articles	vi
Binding of Journals	vii
Reprints of Papers	vii
Bibliography and Abstracts	vii
Medal for Student Members	vii
Advertisements	vii
Appointments Register	viii
Library	viii
Personal Notes and Special Notices	x
Standardization Committee	xi
Seventh Annual Dinner	xi
Award of Medals and Scholarships	xi
Students' Section	xiii

PAGE

Natural Gas in Alberta xiii

American Chemical Society xiv

Department of Scientific and Industrial Research .. xiv

University of Strasbourg xvi

Recent Development in the Art of Cracking, by A. E. Dunstan, D.Sc., F.I.C., F.C.S., and Robert Pitkethley 727

The Rumanian Oilfields, by Lieut. J. H. Blakiston, R.N.R. 775

The Vapour Tensions of the Normal Paraffins, by A. A. Ashworth, M.A., A.M.Inst.C.E. 787

Natural Gas in 1923, by S. J. M. Auld, O.B.E., M.C., D.Sc. 803

Notes on the Cleaning of Tankers, by H. Barringer, M.Inst.C.E., M.I.Mech.E. 810

The Desulphurising of Crude Oil Distillates by Means of Hypochlorite, after the Method of Dunstan and Brooks, by Prof. H. I. Waterman, Ph.D., and J. H. Heimel 812

The Estimation of Lead Tetraethyl in Motor Spirit, by Stanley Francis Birch, Ph.D. 816

Geophysical Surveys as Aids to the Geologist, by E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S. .. 818

Conversion of Petroleum Weights and Measures, by George Sell 821

Liquid Fuels in Canada 824

Discussion on Mr. McCollum's paper, "The Modern Rotary Drilling System," by H. Pennington .. 826

Reviews 828

Current Bibliography, compiled by W. J. Wilson, F.I.C., A.C.G.I. 263A

Petroleum Division, American Chemical Society, Abstracts of Papers 304A

Abstracts, compiled by S. F. Birch, Ph.D., S. Bowman, F.I.C., S. T. Card, B.Sc., R. W. L. Clarke, B.Sc., J. E. Marshall Hall, A.R.S.M., H. Moore, M.Sc., A.I.C., F.C.S., W. S. Norris, Ph.D., R. Pitkethley, F. G. P. Remfrey, B.A., D.Sc., A.I.C., T. A. Smith, B.Sc., F I C, and W. H. Thomas, A.R.S.M. 309A

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English equivalents of foreign weights and measures should be given, and it is suggested that a bibliography of the subject dealt with be appended.

All papers and articles submitted are assumed to be original communications unless otherwise stated, in which case reference to the previous publication should be given.

Members are invited to submit papers to be read at the General Meetings of the Institution, and are specially asked to forward articles for publication in the Journal.

Members desiring to receive advance galley proofs of papers to be read before the Institution should apply to the Secretary, informing him of the address to which the proof is to be sent.

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Orders for extra reprints should be sent to the printers when the manuscript is forwarded to the editor.

Bibliography and Abstracts. A bibliography of current literature is published with each issue of the Journal, together with abstracts of the more important articles and patent specifications, this supplement being paged separately to the Transactions. In order to make this section of the maximum value, members are requested to send any matter which may have been inadvertently overlooked to the editor.

Medal for Student Members. A medal and a prize of five guineas will be awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented a paper of outstanding merit during the session.

Advertisements. A number of Advertisements are inserted in the Journal, and information as to terms, etc., can be obtained from Mr. H. J. Humm, 93 and 94, Chancery Lane, London, W.C. 2. (Telephone No.: Central 8106).

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Library. The Institution's Library may be consulted between the hours of 11 a.m. and 4 p.m. daily.

ADDITIONS TO THE LIBRARY SINCE LAST JOURNAL.

From the American Institute of Mining and Metallurgical Engineers :—

"Production of Petroleum in 1923."

From the Institute of the Czech Polytechnic Highschool of Prague :—

"Report of the Fuel Technology for 1922 and 1923."

Records of the Geological Survey of India. Vol. LV. Part 4. 1924.

Bulletin of the Imperial Institute. Vol. XXII. No. 2. 1924.

Transactions of the Institution of Mechanical Engineers. Vol. I. 1924.

From Mr. F. W. Moon :—

"Natural Indications of Petroleum." May, 1924.

Proceedings of the Iron and Steel Institute. No. 1. Vol. CIX. 1924.

Report of the Empire Motor Fuels Committee, 1924. (Institution of Petroleum Technologists.)

From the Shell Company of California, U.S.A. :—

"The Scientific Basis for Petroleum Refining." By Dr. L. Gurwitsch. Translated by Carl J. von Bibra, Paul D. Barton, and Rosetta A. Barton. 1921.

Summary of Progress of the Geological Survey of Great Britain and the Museum of Practical Geology for the year 1923.

From British Engineering Standards Association :—

Specifications to date.

Fourth Annual Report of the Scientific and Industrial Research Council of Alberta, 1923.

From Imperial College of Science and Technology :—

Calendar for Session 1924–25.

From A. Guiselin :—

(1) Sur la nécessité de Formular les principes fondementaux devant regler l'industrie nouvelle de la transformation, par cracking et catalyse, de matériaux divers en Hydrocarbores volatile.

(2) Utilisation rationelle des déchets organiques en agriculture.

(3) Madagascar et l'industrie pétroliere.

From L. Oertling, Ltd. :—

"The Eotvos Torsion Balance."

From Imperial Mineral Resources Bureau :—

The Mineral Industry of the British Empire and Foreign Countries. Statistics, 1920–1922. Aluminium (including Bauxite and Cryolite), Coal, Coke and By-Products.

From American Society for Testing Materials :—

Year Book. August, 1924.

From Dr. V. Henny :—

"The Cracking of Mexican Gas Oils." By Gustav Egloff.

"The Cracking of Venezuelan Fuel Oil." By Gustav Egloff.

"Simultaneous Skimming and Cracking." By Gustav Egloff.

"Rise of California Petroleum Industry." By Gustav Egloff.

Books for Review :—

From Messrs. Harper and Brothers :—

"The Black Golconda." By Isaac F. Marcosson. 1924.

From Macmillan and Co., Ltd. :—

"The Oil Trusts and Anglo-American Relations." By E. H. Davenport and Sidney Russell Cooke. 1923.

"Wissenschaftliche Grundlagen der Erdolverarbeitung." By Leo Gurwitsch. 1924.

U.S. Geological Survey. Dept. of the Interior :—

Bulletin No. 747. "Geologic literature on North America." 1785–1918. By J. M. Nickles.

Water-Supply Paper. Additional Ground-Water Supplies for the City of Enid. No. 529 B. Oklahoma. By B. Coleman Renwick.

Water-Supply Paper. Surface Water Supply of the United States, 1919 and 1920. No. 503. Part III. Ohio River Basin.

U.S. Bureau of Mines. Dept. of the Interior :—

Reports of Investigations.

Serial No. 2632. August, 1924. An experimental Still for the detailed study of Crude Petroleum. By N. B. Cooke.

Tenth Semi-annual Motor Gasoline Survey. By N. F. Le Jeune and B. A. Landry.

Canada. Dept. of Mines Branch :—

Natural Gas in Alberta. By R. T. Elworthy.

Catalogue from Crane-Bennett, Ltd. :—

No. 5. January, 1924. "Valves Pipe Fitting Steam Specialities."

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. H. D. ADAM has been promoted from Engineer-Lieutenant (Special Reserve), Royal Navy, to Engineer Lieutenant-Commander (Special Reserve), to date from July 4, 1924.

Mr. G. E. STOTT has extended his trip to cover the Oilfields of Sumatra and Java, and does not expect to return to England until late in the year.

Mr. E. A. GARRATT, O.B.E., M.I.Mech.E., M.Am.S.Mech.E., is now Director of Jacobs, Barringer and Garratt, Ltd.

Dr. J. A. L. HENDERSON sailed on September 27 last on s.s. *Empress of France* for a visit to Canada and the United States on professional business and expects to be absent from England until about the third week in December.

Mr. L. P. TIMMINS has been appointed Lecturer and Demonstrator in Drilling at the Birmingham University under Professor Nash.

Mr. W. G. B. COUTTS has again returned to Burma, having left California in May last.

Mr. WILLIAM GRAHAM is home from Sarawak.

Mr. E. H. CUNNINGHAM CRAIG informs us that he has resigned his position as Consulting Geologist to the Cambrian Trust, Ltd.

At the recent General Election Major R. W. BARNETT was re-elected to represent the South-West St. Pancras Borough of London, and Lieut.-Col. Sir ALAN H. BURGOYNE was elected for Kensington.

The Secretary will be glad to receive information as to the whereabouts of the following members: H. L. J. BUTLER, J. A. CHOWN, GEORGES DEMARTEAU, W. E. G. HUDSON-HOBDEN, ALBERT JEFFREYS, G. F. MCKILLOP, A. H. NOBLE and CARL PHILLIPS.

STANDARDISATION COMMITTEE.

The Report of the Standardisation Committee of the Institution has now been published under the title of "Standard Methods of Testing Petroleum and its Products," and copies can be obtained from the Institution Offices at the published price of 6s., or to members of the Institution for distribution, and marked "complimentary," at 4s.

SEVENTH ANNUAL DINNER.

The Seventh Annual Dinner of the Institution of Petroleum Technologists has been arranged to take place at the Connaught Rooms, Great Queen Street, London, W.C. 2, on March 17, 1925, and members are asked to make a note of the date.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

AWARD OF MEDALS AND SCHOLARSHIPS.

At the opening meeting for the 1924-25 Session of the above Institution, which was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C. 2, on October 7 last, the following awards of medals and scholarships were announced.

1. *The Boverton Redwood Medal.*

This medal, which has been presented to the Institution by Mr. Alexander Duckham to commemorate the late Sir Boverton Redwood, Founder and First President of the Institution, is awarded to the author of the paper of the greatest merit on any subject

connected with Petroleum Technology, presented to the Institution during two consecutive Sessions, preference being given to original work.

The award is not confined to members of the Institution, and can be withheld if the Council consider that no paper of sufficiently outstanding merit has been presented.

It has been decided that the award should be made retrospective to 1919, the date of Sir Boverton Redwood's death, and so for the sessions 1919-20 and 1920-21 it has been awarded to M. Paul de Chambrier, of Pechelbronn, for his paper on the "Working of Petroleum by Means of 'Shafts' and 'Galleries'," which was read before the Institution on February 15, 1921.

It is hoped that, if M. Paul de Chambrier can be present, the medal will be presented to him at the Seventh Annual Dinner of the Institution, which is to be held at the Connaught Rooms, Great Queen Street, London, on March 17 next.

As there was no paper of outstanding merit for the Sessions 1921-22 and 1922-23, no award has been made for those Sessions.

2. *Students' Medal and Prize.*

This medal and prize, given by the Institution, is awarded to the student member of the Institution who presents the best paper on any subject connected with Petroleum Technology in any one session.

The medal and prize has been awarded to Lieutenant J. H. Blakiston, R.N.R. (late Student of the Oil Technology Course at Birmingham University), for his paper entitled "The Oilfields of Rumania," which is published in this Journal.

This is the first award of this medal and prize.

3. *The Institution's Scholarships.*

These scholarships are awarded annually, one each to the Royal School of Mines, Imperial College of Science and Technology, London, and to Birmingham University to a third-year student taking the Petroleum Technology Course, who is also a student member of the Institution.

The award is made on the recommendation of his Professors, and is to assist him with his 4th year studies.

The award to the student at the Royal School of Mines has been made to Mr. Ernest Clark, and the award at Birmingham University to Geoffrey Cotton.

STUDENTS' SECTION.

A party of Student Members of the Institution of Petroleum Technologists recently visited the British Empire Exhibition at the invitation of Messrs. Vickers, Limited, and received an instructive demonstration of rotary drilling at the firm's electrically driven drilling rig in the grounds. The sequence of operations involved in the adding of a new length of drill-pipe to the column, pulling the drill-pipe and the method of changing bits was illustrated, and the uses of various types of devices were shown and explained. The party were later entertained at tea on Messrs. Vickers' stand in the Palace of Engineering, where they were shown the Oil Refining Exhibit and the model of the fusion rotary retort in the Research Department.

NATURAL GAS IN ALBERTA.

THE High Commissioner for Canada is advised by the Dominion Department of Mines that the Mines Branch is issuing shortly a 35-page booklet by Mr. R. T. Elworthy in regard to the Natural Gas Resources of Alberta, this being an advance section of the report on Mines Branch investigations of mineral resources and the mining industry during 1923.

A thorough survey of the petroleum and natural gas resources of Canada was made in 1912 and 1913, and an exhaustive report covering the results of these investigations was issued by the Mines Branch in 1914. During the last decade, however, many large flows of natural gas have been found in Alberta, and the existence of extensive fields indicated in the earlier report has been confirmed. The present pamphlet is, therefore, of timely interest, as it gives reliable information, hitherto unprocurable, on these fields, the volume of the gases available and their character. The report is based on an investigation of the possibilities of the development of the natural gas, gasoline and carbon black industries in Alberta. These industries are firmly established in the United States and are of great importance. The principal gas areas are described, with brief reference to the geological formations underlying them, and the volume, pressure, composition and gasoline content of gases from representative wells are recorded. Particular attention has been paid to the commercial possibilities of natural gas, gasoline production, the manufacture of carbon black and to the extraction of helium, and detailed information is now available with regard to the present situation and the probable future of each of these

industries in Canada. The names of the chief companies operating in these areas and the locations of their properties are listed. Numerous reports of analyses and comparative tables complete the booklet and make it of exceptional value to those interested in the establishment of the natural gas industry.

Copies of the booklet, when published, will be available on application to the High Commissioner for Canada, Kinnaird House, Pall Mall East, London, S.W. 1, or to the Department of Mines, Ottawa, Canada.

AMERICAN CHEMICAL SOCIETY.

The meeting of the Petroleum Division of the American Chemical Society at Ithaca, New York, on September 10 and 11, 1924, was well attended. In the absence of the Secretary, Mr. G. A. Burrell, Mr. W. A. Gruse acted as Secretary pro tem.

Abstracts of the papers submitted to the meeting will be found on pages 304A–308A of this JOURNAL. Considerable discussion took place, especially on the papers relating to the removal of sulphur from petroleum distillates and on crank case dilution.

The research programme, under the direction of Dr. Manning, continues to make progress and it is probable that a report will be presented at the Spring Meeting of the Division.

The following officers were elected for the coming year :—

Chairman . . .	R. R. MATTHEWS.
Vice-Chairman . .	R. E. WILSON.
Secretary and Treasurer .	G. A. BURRELL.
Executive Committee .	W. F. FARAGHER.
	C. O. JOHNS.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

LOW TEMPERATURE CARBONISATION OF COAL.

The Department of Scientific and Industrial Research, Old Queen Street, S.W. 1, is prepared to undertake in approved cases tests on plants for low temperature carbonisation. The objects of the test are to ascertain the quality and quantity of the yields of coke, tar oil, gas and ammonia, the throughput of the plant, working temperatures, and general ease and reliability of working. No charge will be made by the Department in respect of the tests, but applicants

will be required to comply with certain conditions and to sign an Agreement embodying the terms on which this offer is made. Forms of application may be obtained from the Secretary, Department of Scientific and Industrial Research, 16, Old Queen Street, Westminster, S.W. 1. The nature of these conditions can be ascertained from the following particulars, but the Department reserves the right to add to or alter them as may be thought necessary.

(1) Applicants will be required, before the Department can undertake a test, to supply full information as to the nature of the plants and results obtained and to afford facilities for the inspection of the plant by one or more officers of the Department and generally to satisfy the Director of Fuel Research that the plant is giving reasonably good results and is of such a size that its performance will be comparable with that of a similar plant operating on a commercial scale.

(2) Tests will be under the continuous supervision of such members of the Fuel Research staff of the Department as the Department may decide, who may take as samples such amount as they may consider necessary both of the coal used and of the products.

(3) Applicants must at their own expense provide all necessary facilities, including all material, staff and labour required for running the plant, and for such assistance in taking samples and measurements as may be required by the Department or its officers supervising the test.

(4) Until the information referred to in paragraph (1) above has been supplied and a preliminary inspection of the plant has been made, it is impossible to state what facilities will be required or to give any indication of the programme or possible duration of the test, which may vary from several days to several weeks according to circumstances.

The necessary facilities will in any event include proper arrangements for taking such measurements as will give a satisfactory weight balance between the input and output of the plant.

(5) Applicants will be permitted to have a representative present during the test who will be allowed to check any weights or measurements forming an integral part of the test.

(6) The decision of the supervising officer of the Department in charge of the test will be final in regard to all questions relating to the duration and conduct of the test and all weights, measurements and other matters in connection therewith.

(7) The Department reserves the right to publish a report on the test at any time at its discretion, but will before so doing consult the applicants, and any views the latter may express will receive

consideration. A copy of the report will, at the request of the applicants, be furnished to them free of charge. Applicants will not be entitled to publish or communicate to third parties such report or any extract from or allusion to it without the consent in writing of the Department. Such consent may be conditional.

Report of Test on Parker Plant.

A report by the Director of Fuel Research on the test of a "standard unit" of the "Parker" plant for the low-temperature carbonisation of coal installed at the Barugh, Barnsley, works of Low Temperature Carbonisation, Ltd., can be obtained from H.M. Stationery Office, or through any bookseller at the price of 9d. net, post free 10d.

UNIVERSITY OF STRASBOURG.

National Petroleum and Liquid Fuel School.

We have received the following notice from the Petroleum Department of the Board of Trade:—

According to the *Information Financière* of October 29, 1924, an agreement has been reached between the Petroleum Department of the Ministry of Commerce, the Ministry of Public Instruction and the University of Strasbourg for the institution at Strasbourg of a National Petroleum and Liquid Fuel School.

The new school, which will be opened in November, 1924, will consist of three principal sections devoted to geology, chemistry and the working of oil fields.

It is intended that the school shall gradually take the place of the existing Petroleum Institute, the organisation and scope of which will be greatly enlarged. The school will be temporarily attached to the Science Faculty of the University of Strasbourg, and will only take its final form in October, 1925, when it will enter into occupation of its new buildings.

Considerable funds have been collected by the patronage committee formed by the Strasbourg Chamber of Commerce, and the expenditure on the necessary buildings will be met by donations from the State, the town of Strasbourg, which has given the land, the *Conseils Généraux* and the Chambers of Commerce of the Bas-Rhin and the Haut-Rhin, the Pechelbronn Oil Company, etc.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The Eightieth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts on Tuesday evening, October 7th, 1924, Mr. Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng., President, occupying the chair.

The Secretary read the following list of new members and transferences made since the last meeting:—

Members.—William Henry Cadman, Ernest Hope Crush, Albert Fauck, The Rt. Hon. Lord Forres, William Owsley George, Gordon Cairns MacLaran, Jan Martynik, Antonio Mora, George Henry Sargent, Benjamin Schang.

Transference to Member.—Thomas Sutton Bowman, Stanley Edward Bowrey, George Samuel Hay, John Thomson Hayward, Len Riley Roberts.

Associate Members.—Robert Ashley Baldry, Jan Lambertus Benard, Reuben Charles Blake, Alfred Edward Day, Alejandro Figueroa, Ernest Edward Garrard, Kenneth Brand Harper, James Edmund Earl Jenkin, George Lewis Kennaby, Francis Alleyne Marr, Jack Edward Miller, Eustace Tanfield Vachell, Joseph Pierre deVerteuil, Frank Clifton Waters.

Transference to Associate Member.—Walter Edgar Aylwin, Bernard George Banks, Robert Louis Charles Bleeck, Gwyn Elias, Sydney John Fortescue, Ronald Sowerby Teale.

Students.—Percival Driver, Maurice Arneil Rust, Geoffrey Stewart Taitt.

Associates.—Francis Edward Eyles, James Tordiff Hayton.

The President having, on behalf of the Institution, welcomed the new members, said that in opening the Session 1924–25 he had a few announcements to make. The Boverton Redwood Medal, presented by Mr. Alexander Duckham, and which was presented for the paper of greatest merit in two consecutive sessions, had been awarded to M Paul de Chambrier, for 1919–20 and 1920–21, and would be presented at the Annual Dinner. For 1921–22 and 1922–23 no paper was considered of sufficient merit and no award was made. The Students' Medal and Prize for the last session had been awarded to Lieutenant J. H. Blakiston, a former student of Birmingham University, now in Venezuela, and would be forwarded to him. The Students' Scholarship at the Royal School of Mines

had been awarded to Mr. Ernest Clark. He further desired to announce that a Students' Meeting would be held at Aldine House at 6 p.m. on October 21st, when a paper on "The Chemistry of Petroleum" would be read by Mr. H. S. Garlick.

The following paper was then read:—

Recent Development in the Art of Cracking.

By A. E. DUNSTAN, D.Sc., F.I.C., F.C.S., and ROBERT PITKETHLY (Members).

It is now eight years since Dr. F. B. Thole, Mr E Lawson Lomax and one of the present authors surveyed the problems incident to cracking.[1] Much oil has flowed through the pipe-lines since then, and the present moment is a convenient one for a general consideration of the situation, seeing that the art is in process of being standardised.

Surveying the typical examples of cracking processes dealt with in the sequel and the subject in general, there are certain outstanding points of interest. In the first place, vapour phase processes working under practically atmospheric pressure have not been particularly successful; losses are high and the products are poor in quality. On the other hand, exceedingly high pressure processes have not advanced far beyond the development stage. Most of the processes which have been utilised to any extent operate under comparatively moderate pressures. General observations appear to point to the conclusion that, provided the pressure is sufficient to maintain the oil under operation mainly in the liquid phase, there is no particular advantage in moderately higher pressure, as far as the quality of the product is concerned, as oils converted at pressures between 350 and 700 lb. appear to have similar characteristics. Considering extremely high pressure processes like that of Bergius[2], it is apparent that hydrogen disappears in certain cases, but it is questionable if the hydrogen is contained in the liquid products of lower boiling point. Waterman's work[3] on this subject is particularly interesting.

The question of temperature in liquid phase cracking is decided by the particular oil under treatment and the amount of spirit desired, as there appears to be a definite relationship between the three variables—time, temperature and yield. The percentage of spirit obtained after the oil has reached definite cracking temperature appears to double itself, within limits, for an increase of

[1] *Journ. Inst. Petr. Techn.*, III., 9, Dec., 1916.
[2] Brit. Pat. 4574 of 1914.
[3] *Journ. Inst. Petr. Techn.*, X., 45, p. 670, Sept., 1924.

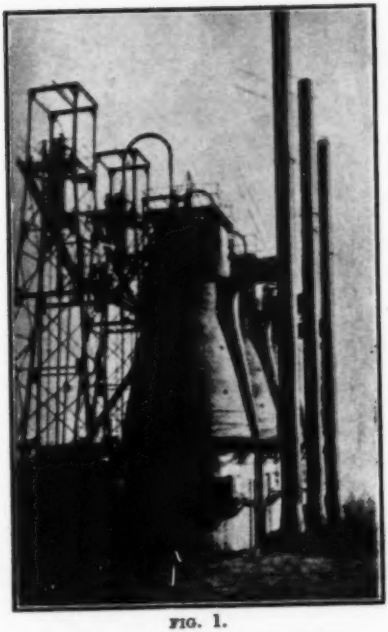

FIG. 1.

A BATTERY OF THREE FLEMING UNITS.

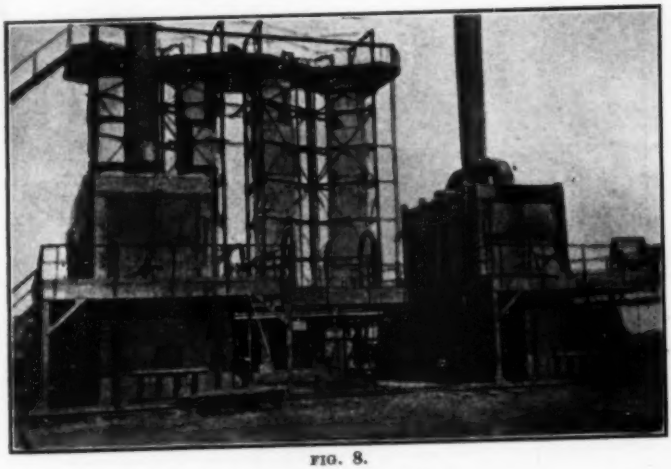

FIG. 8.

CARLETON ELLIS PLANT.

THE CRACKING COILS ARE ENCLOSED WITHIN THE VAULT-LIKE CONSTRUCTION BEHIND THE STEEL DOORS OF EACH UNIT. THE UPRIGHT CYLINDERS IN THE REAR ARE THE SOAKING DRUMS. STILLS AND FRACTIONATING EQUIPMENT ARE NOT IN VIEW.

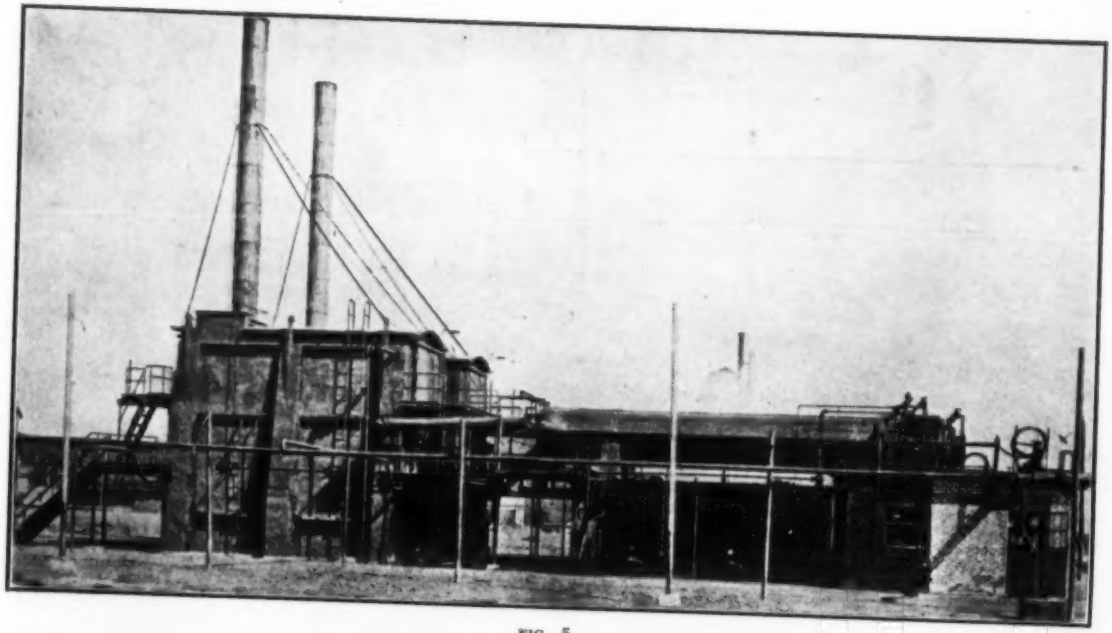

FIG. 5.

A COMPLETE TWO UNIT INSTALLATION OF THE CROSS PROCESS.

temperature in the neighbourhood of 10°C. In the same way, when the rate of pumping is halved, or the time of reaction doubled, the same increase in spirit content is noted.

There has not been a great advance in our knowledge of cracking from a chemical point of view during the last few years. The problems connected with cracking processes have been more of an engineering quality. The most urgent problem to the majority of refiners is the elimination—or at any rate the diminution in quantity—of coke, in order to allow plant to run continuously without having to close down periodically. Bergius claims to have successfully overcome this problem, but, to the majority of others the question is definite, and it is questionable if coke can be eliminated without hydrogenation brought about by one method or another.

Surprisingly little progress has been made in the examination of the residues left after the cracked gasoline has been removed from the synthetic crude oil. The work of Brownlee (v. i.) may be instanced as an attempt to explore the possibilities of this material, and investigators will do well to bear in mind that here is a reactive material of unknown constitution, the knowledge of which would probably amply repay intensive research.

Nothing has arisen in the interim to cause us to modify the views discussed in the previous paper to which reference has been made. The kinetics of pyrolysis still remain in a sketchy and unsatisfactory condition, and it is not surprising that this should be so when it is realised what little exact knowledge we have of the decomposition of even the simplest hydrocarbons.

We now proceed to discuss a few processes which we have personally investigated, and these have been selected, firstly, because they exhibit interesting difference in procedure, and secondly, because they show promise of leading to a cracking technique and process which shall be as standardised and simple as a still or any other piece of familiar refinery plant.

Vapour Phase. Atmospheric Pressure.

Ramage's method[4] of cracking is a typical vapour phase process (*cf. Journ. Inst. Petr. Techn., III.* 1916, p. 36, for description of Noad, Hall's and Lucas' plants). It consists of passing the vapour of the hydrocarbon over a reducible metallic oxide such as iron oxide, regulating the temperature and the time of contract in order to oxidise a part of the hydrocarbon with incomplete reduction of the oxide whereby separation of carbon is substantially prevented.

[4] Brit. Pat. 106,080.

Ramage uses the following equations to illustrate his description of the process:—

1. $C_nH_{2n}+{}_2+Fe_2O_3=CnH_{2n}+2FeO+H_2O.$
2. $C_{16}H_{32}\rightarrow 2\ C_8H_{16}\rightarrow 4\ C_4H_8\rightarrow 8\ C_2H_4.$
3. $C_2H_4+2\ Fe_2O_3=2\ C+4\ FeO+2\ H_2O.$
4. $C+Fe_2O_3=2\ FeO+CO$ (550° C.).
5. $CO+Fe_2O_3=2\ FeO+CO_2$ (550° C.).
6. $H_2O+2\ FeO=Fe_2O_3+H_2$ (500–600°).

The hydrogen eliminated in (6) is alleged to be responsible for the hydrogenation of the unsaturated hydrocarbons which are produced in the main operations (1) and (2).

Ramage[5] claims further use for his process in treating aromatic hydrocarbons containing one or more alkyl groups for the replacement of the alkyl group by hydrogen, thus converting toluene and xylene into benzene at a temperature approximating 700° C. in presence of a catalyst comprising a lower oxide of iron. He claims particularly that whatever the source of the gas oil operated on, there is a consistency in the properties of the product.

In 1922 the process had developed on a reasonable scale and was past the experimental stage. Gas Oil from Persian and Mexican Crudes had been successfully cracked. The gas loss was by no means excessive compared with other vapour phase processes, but would more than suffice for the firing of the plant. The plant, however, could not handle oils other than distillates, and the product did not differ markedly from other cracked spirits. The same refining losses were met with as are experienced with similar products. Considerable interest was attached to the condition of the cracking tubes. One tube which had been regularly used over eighteen months after opening up showed no signs of wear and tear.

An experimental plant operating at Detroit consisted of a horizontal gas-fired still, capable of working up to 50 lbs. pressure per square inch. The oil was introduced into the still and kept boiling at a pressure of 4–5 lbs., the vapours being led to the cracking tube, which consisted of 20 ft. of 4-in. iron pipe filled two-thirds with powdered hæmatite. Dry steam supplied by a small vertical gas fire boiler of 5-gallons capacity and at 6 to 7 lbs. pressure was led into the same end of the cracking tube as the oil vapours, the flow of each being regulated by gate valves pierced with holes of known diameter so that the orifices were as 4 : 1 oil to steam.

[5] U.S. Pat. 1,365,849 of 1921.

The cracking tube was heated electrically in two 10 ft. sections and insulated with asbestos powder. A blind tube 3 ft. long was fitted through each of the flanged ends for pyrometers. After passing through the cracking tube the vapours passed through a short 1 in. tube to an air cooled catch-pot, where heavy uncracked oil was trapped and thence through a water-cooled condenser to gas-tight receivers fitted with gauge glasses and drain cocks. The uncondensed gases were scrubbed with gas oil and passed through a meter. The heating of still, boiler and cracking tube were commenced simultaneously with control valves closed. When the pressure of still and boiler reached 6 and 4 lbs. respectively and temperature along the whole cracking tube was at 550° C. the control valves of still and boiler were opened wide and the flow was automatically controlled by the pierced gate-valves. The flow of oil amounted to about three gallons per hour. On first introducing the vapours into the cracking tube the temperature of the first half fell to 450° C., then rose slowly to about 480° as the boiling temperature of the oil went up. In the second half of the tube the temperature commenced to rise at once, going up to 650° C., and the external heating was discontinued since the temperature maintained itself by means of exothermic reactions occurring within the tube. Uncondensable gas amounted to about 20 per cent. of the oil, and the reactions took place at practically atmospheric pressure so that obstruction could be detected at once by the pressure gauges.

On the commercial plant at Tulsa each furnace comprised a nest of 63 cracking tubes, 20 ft. by 6 in., arranged in rows of seven tubes, and the nest is fed by headers from the vapour line. Air blowing for a few minutes every 24 hours kept the hæmatite free from sulphur.

The life of the hæmatite seemed to be indefinite, the experimental tube at Detroit having worked for over twelve months without being opened. During this period all sorts and conditions of oil had been run, but on opening the tube no trace of coking could be seen.

As a whole the plant appeared easy to run and working costs should be low.

A typical run conducted with heavy fuel oil on the Detroit plant gave the following figures :—

K.W. for heating=8 per hour.
Temperature.—1st half of tube, maximum 680° C., minimum 500°.
,, 2nd half of tube, maximum 710° C., minimum 600° C.
Oil processed=13·8 gallons.
Condensate=8·15 gallons.

Condensate boiling below 200° C.=3·18 gallons=39 per cent.
Spirit from scrubbers=2·0 gallons.
Volume of gas produced=363 cubic feet.
Grand total of motor spirit below 200° C.=3·18+2=5·18 gallons.
Oil converted into motor spirit=8·08 gallons.
Per cent. conversion to motor spirit=64 per cent.

Loss of oil in cracking is	19·8	per cent. (includes gas).
„ „ washing is	0·8	„
„ „ redistilling is	2·0	„
Total loss ..	22·6	„

Analysis of the packing in the tube appeared to vitiate the claim that ferrous oxide was the chief component.

The spirit prepared by this process had the characteristic smell of cracked spirit and on slow evaporation yielded a gummy residue. Specific gravity, boiling range and degree of unsaturation compared closely with those of spirit made by other vapour cracking processes.

A minimum of 70 per cent. recovery should be obtained with efficient scrubbing of the gas.

Ramage claimed that he obtained a new class of cyclo-paraffin, but when compared with other cracked spirits his contention appeared to have no foundation. Chemical analysis point to the conclusion that instead of being a spirit largely composed of saturated compounds the proportion of unsaturated bodies exceeded 50 per cent.

Further tests were carried out later, and the claim that oil in presence of steam passing over a contact mass of hæmatite converts it into ferrous oxide has not been substantiated, and in fact a contact mass of metallic iron under the same conditions produces identical results, for clearly the equilibrium attained will be the same whether one starts with the metal, any of its three oxides, or its carbonate.

To connect vapour phase with liquid phase processes we must mention processes of the pressure still type as these are the forerunners of the modern liquid phase processes. The cracking and distillation of the products take place within the still, at pressures above atmospheric. There is a great loss of heat on account of the necessary refluxing. For instance, it is estimated that, in the Fleming plant, the amount of oil condensed in the dephlegmator is six or seven times the amount of vapour allowed to escape to the condenser. Considerable carbon troubles are experienced in all processes of this type, nevertheless the bulk of cracked spirit produced in the United States is manufactured by them.

To this class the Fleming process[6] belongs. It is usually constructed in 200 barrel units, which can be multiplied to form

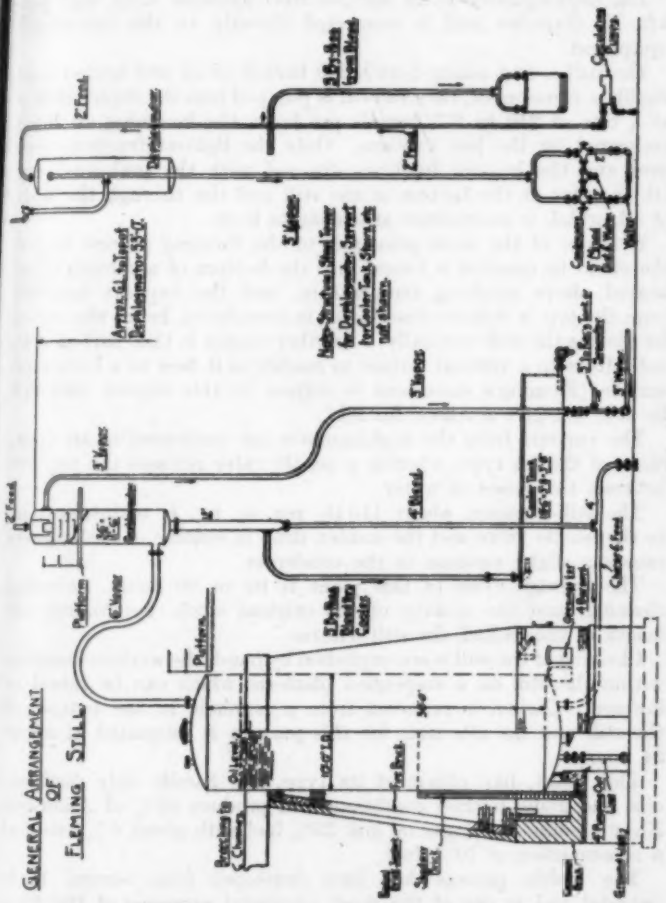

FIG. 2.

large batteries. Each unit consists of an upright still made from hammer welded steel 1 in. thick, 30 ft. high and 10 ft. in diameter. Heat is generated by four burners set round the still at equal

[6] The Refined and Nat. Gas Manufacturer. Vol. 2, No. 3 (1923). Vol. 2, No. 10 (1923).

distances, the shell of the still being protected by firebrick walls opposite the direct flame.

The dephlegmator is an upright steel cylinder 12 ft. high and 3 ft. in diameter and is connected directly to the condensing equipment.

The still is first charged with 300 barrels of oil and heated until distillate comes over, then raw oil is pumped into the dephlegmator at a rate of 250 to 275 barrels per hour, the incoming oil being preheated by the hot vapours. Only the lightest fractions pass over and the heavier fractions descend with the preheated raw oil, to enter at the bottom of the still and rise through the body of oil, which is maintained at a definite level.

It is one of the basic principles of the Fleming process that if the oil to be cracked is forced into the bottom of a column of oil heated above cracking temperature, and the vapours removed from the top, a definite time factor is introduced, hence the reason for placing the still vertically. Another reason is that carbon does not adhere to a vertical surface so readily as it does to a horizontal surface (Fleming's statement is correct in this respect although he does not give a reason for it).[7]

The vapours from the dephlegmator are condensed in an apparatus of the jet type, wherein a needle valve releases the vapours between two cones of water.

The still-pressure, about 110 lb. per sq. in., is maintained up to the needle valve and the sudden drop in volume of the vapours causes a slight vacuum in the condenser.

The average cycle of this plant is 60 to 80 hours, including cleaning, and the quality of the original stock determines the length of time which the still will run.

Cleaning of the still is accomplished by hand, the workers standing within the still on a suspended platform which can be raised or lowered. Carbon is removed from a manhole in the bottom of the still and the idle time for this purpose is estimated at about 24 hours.

This plant, like others of its type, can handle only distillate oils, and under normal conditions can produce 35% of American Navy gasoline, 35% gas oil and 25% fuel with about 5% loss and a consumption of 10% fuel.

The Dubbs process[8] has been developed from several basic patents[9] and is one of the most successful processes of the two-phase type wherein the oil is cracked in tubes in the liquid phase. At the moment there are 113 units of the plant in operation or under construction.

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[7] See Dr. Thole's remarks under discussion, p. 765.
[8] Universal Oil Products Co., New York.
[9] U.S. Pats. 1,123,502 of 1919 and 1,470,353 of 1924.

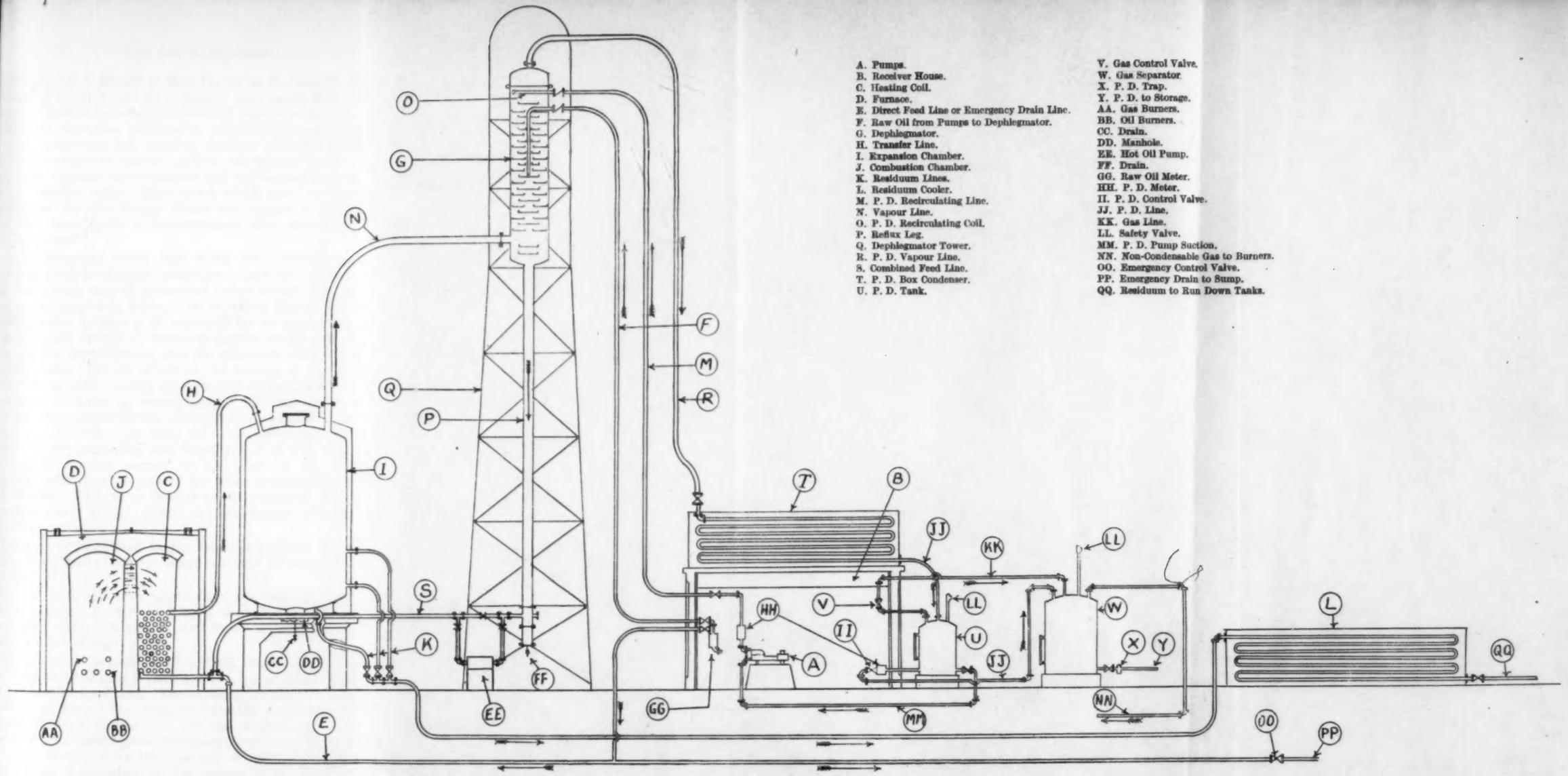


FIG. 3.

FLOW CHART, DUBBS PROCESS.

The process is simple in that the oil to be cracked is pumped through a heating coil in a furnace and passes into a hammer welded reaction chamber, wherein all coke is collected and from which the residuum produced is continuously withdrawn. The vapours pass from the reaction chamber into the dephlegmator, which separates the heavier oil from the lighter cracked vapours. The light vapours are condensed and the heavier fractions return to the heating tubes. The model which has been lent by the proprietors for this lecture shows the layout of the plant, and the flow chart shows in diagrammatic form the arrangement of the equipment.

In the Standard Dubbs unit of 500 bbls. capacity per day the charging stock is pumped continuously and at a uniform rate by the feed pump, and is discharged either directly into the heating coil in the furnace or through the overhead line to the top of the dephlegmator, wherein it is preheated by the condensing vapours. The feed may be split by means of control valves, part of it going through the dephlegmator and the remainder direct through the heating coils. The oil enters at the bottom of the heating coil and flows upward, passing through fifty 4-inch tubes 30 feet long, connected in series by return bends. The furnace is side fired and has two compartments, a combustion chamber and a heating chamber. The hot gases from the combustion chamber pass into the chamber containing the heating coil at the top and flow downwards counter current to the flow of oil. The double chamber is designed to protect the tubes from the direct flame of the furnace. The oil is heated to the required cracking temperature, about 450° C., before it is discharged into the reaction chamber.

Cracking is completed in the reaction chamber without additional heat, heavy lagging being sufficient to maintain the temperature.

The oil separates into vapour and residuum fuel oil and the carbon liberated by the cracking is deposited in the chamber to form coke. The residuum is withdrawn continuously through a cooler to fuel storage.

The reaction chamber is 10 feet in diameter by 15 feet high and 1½ inches thick, and is provided with run-off pipes, for successive use as the coke level rises. The capacity for coke of each chamber is about 30 tons. The vapours from the reaction chamber are transferred by a vapour line into the dephlegmator, which also acts as a heat exchanger as the temperature in the dephlegmator is mainly controlled by the quantity of cold raw oil introduced. The average temperature at the bottom of the dephlegmator is about 395° C. The condensed heavy oil and the raw oil, pre-

heated to about 300° C., pass from the dephlegmator down the reflux leg via the feed line to the cracking tubes.

The light vapours rise to the top of the dephlegmator and are discharged through a line into the condenser. The condensate and the uncondensable vapours flow into the pressure distillate receiver. Up to this point the entire system is under a uniform pressure of about 140 lbs./sq. in.; thereafter the gas separates at atmospheric pressure from the distillate and is used as fuel. In the process control temperature recording instruments are placed in the furnace, in the transfer liquid to the reaction chamber, in the cracked vapour as it leaves the dephlegmator, and in the residuum leaving the reaction chamber. Pressure is recorded by a gauge on the pressure distillate receiver. Oil meters measure the raw oil and a gas meter measures the amount of gas produced. It is claimed for the Dubbs Process that it has the ability to crack any liquid hydrocarbon from kerosene distillates to heavy residues such as Panuco Residue. There is no appreciable formation of carbon in the heating coil, and the length of the run is determined by the capacity of the reaction chamber to store coke. In the light of many serious results which have ensued from the operation of cracking plants the safety of the process is claimed. In a 500-bbl. unit only 10 to 20 bbls. of oil are in the coil subjected to heat, but not to direct flame, and a limited quantity (about 20 bbls.) is maintained in the reaction chamber which is outside the heating zone.

The Dubbs process is the only process which is successfully cracking commercial fuel, residues or topped crude direct without pre-treatment or distillation.

Distilling fuel oil and cracking the distillate is not the same as cracking fuel direct, as the residue on distillation is pitchy, with only 50 to 60 per cent. distillate suitable for cracking. Whereas running the fuel oil direct yields 40 to 50 per cent. Navy gasoline, 25 to 50 per cent. gas oil and the balance coke and gas. If residuum is desired this can be produced from the reaction chamber and is suitable for fuel.

The coke is dry and hard and a good commercial fuel. It is suitable for briquetting, and in most instances without a binder.

The one unit standard plant is estimated to cost about £15,000, without tanks, steam and water auxiliaries, etc.

The control of the plant is simple, and two or three men per shift are capable of operating two units with total capacity of 1000 bbls. per day. Once the operating conditions are fixed there is little or nothing to do until the run comes to a finish.

As an example of the work done by the plant we quote the cracking of Mid-continent fuel oil in a number of typical com-

mercial runs. The fuel used was the residue after distilling off the gasoline, kerosene and gas oil, and ranged in specific gravity from 0·900 to 0·912.

The pressure distillate received represented 61 to 69 per cent., having a specific gravity 0·760 to 0·778. This pressure distillate on treatment with acid and soda and redistillation gave 40 to 42 per cent. of American Navy Specification gasoline, the remainder

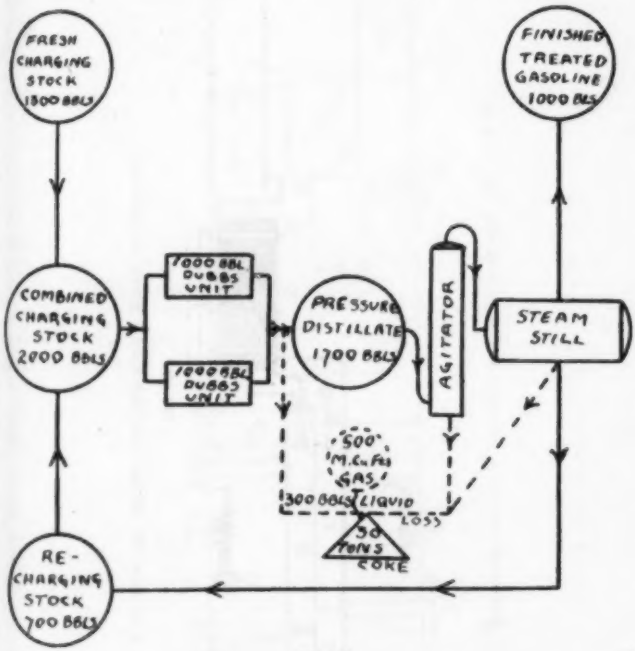


FIG. 4.

DUBBS CRACKING PROCESS OPERATING ON MID-CONTINENT FUEL OIL. NO RESIDUUM RUN WITH RE-CYCLE.

being kerosene and gas oil suitable for further cracking. The residuum fuel was an excellent fuel, having a lower viscosity than the original, and amounted to between 25 and 36 per cent. of the raw stock. The specific gravity ranged from 0·959 to 0·979. The coke produced varied between 16 and 26 tons per run. The gas and coke together amounted to 4½ to 6 per cent. Fuel

consumption about 2 per cent. of liquid fuel and the uncondensable gas produced and burned about 4 per cent.=total 6 per cent. The plant runs continuously for about five days on steam.

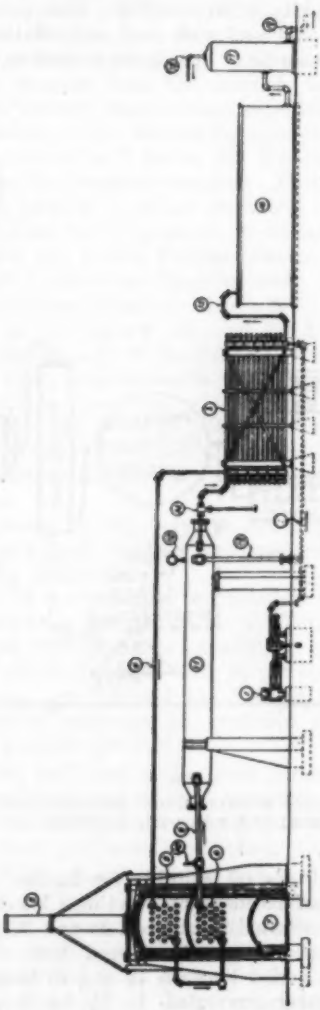


FIG. 6.

DIAGRAM OF CROSS PROCESS USING HEAT EXCHANGER.

The Cross process[10] was originally a vapour phase cracking process which developed into the present method when the advantages of liquid phase cracking became known.

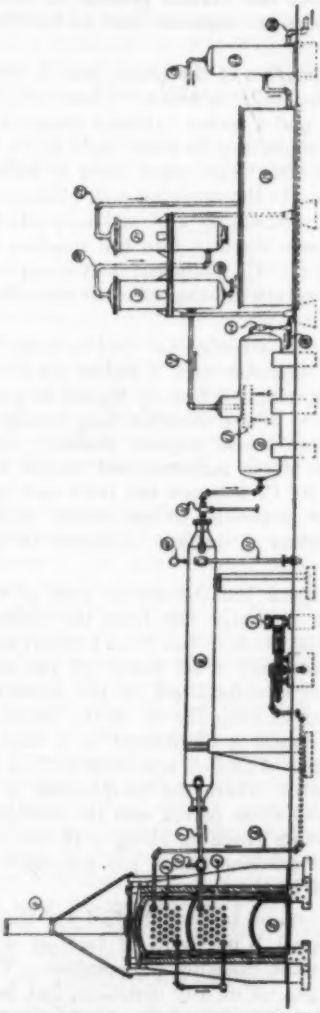


FIG. 7.

DIAGRAM OF CROSS PROCESS USING VAPORIZER AND TOWERS.

[10] U.S. Pats. 1,423,500 and 1,437,229 of 1922.

It differs from the Dubbs process in the form of the apparatus, the pressure and temperature conditions, and the patentees do not advise the use of heavy fuel residues without a preliminary distillation. It resembles the Dubbs process in so far as the heating and reaction zones are separate, and no heat is applied to the reaction vessel.

In the commercial operation of the plant, heat is applied to the oil in tubes placed horizontally in series. These tubes are 24 feet long, 3 inches internal, and 4 inches external diameter. They are arranged in two banks, containing 45 tubes each, above the furnace, and form a continuous coil. The upper bank of tubes acts as a preheater and the lower is the cracking coil. The oil is pumped downward through the preheating coil and upwards through the cracking coil; then passes directly into the reaction chamber at a temperature of about 470° C. Sufficient heat is applied to the oil to maintain its temperature in the reaction chamber until the reaction is complete.

The reaction chamber is a horizontal steel cylinder 40 feet long by 38 inches internal diameter and 3 inches thick. No heat is applied to the chamber, but it is heavily lagged to prevent loss of heat, and the oil is held in this chamber long enough to establish equilibrium between liquid and vapour phases; this period is estimated to be about fifteen minutes, and results in a drop in temperature of about 50° C. between the inlet and outlet. It is stated that coke is not deposited to any extent in the cracking tubes, and the deposition is mainly confined to the reaction vessel.

Under normal conditions the amount of coke produced is less than 1 per cent. The discharge line from the reaction vessel is set at the liquid level and controls this level without any automatic device other than an ordinary relief valve. A pressure of 600 to 700 lb. per square inch is maintained on the system in order to prevent distillation and to keep the oil in the liquid phase. The oil from the reaction vessel is discharged to a vapour separator wherein a certain amount of fuel oil is collected. The vapours then pass to the dephlegmator, where the temperature is regulated to yield the required specification petrol, and the condensed fractions are withdrawn for further cracking along with raw oil stock. A condenser liquefies the gasoline and a gas separator removes the permanent gas formed in the process.

Sufficient gas is produced to provide fuel for the operation of the plant; an additional 1 per cent. of fuel oil is necessary to bring the plant up to the cracking temperature. The plant will operate on kerosene, gas oil or any distillate, but heavy fuel oils are not recommended on account of the excessive amount of coke

deposited in the reaction vessel. By combining a simple type of pipe still with the main plant, residue may be processed.

The plant can run continuously on gas oil for about a week, or on kerosene for about three weeks, without cleaning.

The throughput of a modern double unit Cross plant is 2000 bbls. per day, and it is stated that a yield of 33 per cent. of Navy gasoline can be obtained in one cycle from gas oil, 40 per cent. of the same quality from kerosene distillates, and 20 to 25 per cent. from fuel oil.

The total yields in running gas oil and recycling the residue, without the addition of fresh oil, are recorded by Cross as follows :—

Gasoline (Navy)	64·8 per cent.
Fuel Oil	24·8 „
Loss	10·4 „

But as usually operated the production is of the order already stated, and the yield on recycling the oil is about equivalent to the cracking of an equal quantity of original oil.

Dr. Roy Cross accentuates the factor of safety in cracking plant, and is of the opinion that cracking problems are not so much chemical as engineering problems, and for this reason he has taken care as far as possible that his plant should be able to withstand the conditions of temperature and pressure under which the operation is conducted.

The latest development in the well-known Carlton Ellis[11] cracking method is an instance of a parallel development by experience and observation towards the same object, for it is our opinion that vertical reactors will be more the rule than the exception in the future. The process is licensed by the Standard Oil Company (N.J.), and is similar to other plants using the process, but the Invincible Oil Company has taken into account the different classes of crude or topped oil it will use, and has constructed a plant sufficiently flexible to allow any of these oils to be treated for the production of commercial gasoline. The plant is in two units, each of which is capable of a daily throughput of 2000 barrels.

The oil is fed into coils under a pressure of 350 lb., and natural gas is used as fuel. The oil usually passes through the coils at a rate of 5000 gallons per hour into the " soaking drums," which are upright cylindrical reaction vessels. The quality of the crude stock determines how long the oil must remain in these drums, but it is held long enough to allow the time factor to have its effect, and is then released steadily, passing into horizontal vaporising stills, where the cracked products vaporise and pass overhead into the fractionating columns. It is stated that the

[11] *Ref. and Nat. Gas Manufr.*, 3, 8, 1924.

gasoline produced can be treated as straight run spirit and does not require blending to bring it to commercial specification. It is claimed that a residuum fuel oil is obtained, after the gasoline has been removed, which is free from suspended carbon of excellent quality as a fuel oil.

There are two cracking coils each with a capacity of 2000 barrels per day, and the flexibility of the equipment is due to the "soaking drums" or upright reaction chambers, of which there are two to each system. They can be operated singly, in pairs, or can be omitted, according to the treatment necessary. On raw material which gives considerable quantities of coke the system can work on one chamber while the other is being cleaned, or the amount of coke can be divided by using both. On stocks requiring less time for cracking one drum is sufficient, and when it is desired to lower the viscosity of a fuel oil only, the drums may be by-passed, without coming into action. The length of the running period varies with the crude stock and the products desired, but the average is six days on gas oil or crude. Likewise the yield of gasoline will vary, but can be easily controlled.

This particular plant departs from the common practice of carrying pressure throughout the system, and is practically a combination of a cracking still and a crude still, and it is possible to see the quantity of oil that each still is running without relying on mechanical measurements.

The plant has been designed to give the utmost from an economical, as well as a safety in working, point of view. Heat economisers are used wherever possible, resulting in the ingoing oil entering the heating coil at a temperature of about 250° C.

The Auld, Dunstan and Herring process[12] is the direct result of several years' work which started when Dr. Thole and one of the present authors observed that the gelling property of heavy residues was to a great extent destroyed by heat treatment under pressure.

The object of research work at that time was the rendering of the residue available as a fuel, which would pass the standard tests. Later, the production of petrol along with liquid residue was required.

Further investigations led to the erection of a small plant, which was altered and modified until it bore little resemblance to the original.

The process is substantially a liquid phase operation throughout, and has advantages over the vapour or dual phase systems.

The development of the plant has been governed almost entirely by the following points as basic principles:—

(1) The pressure should be sufficiently high substantially to maintain the oil passing through the plant in the liquid condition

[12] Brit. Pat. 220,664 of 1924.

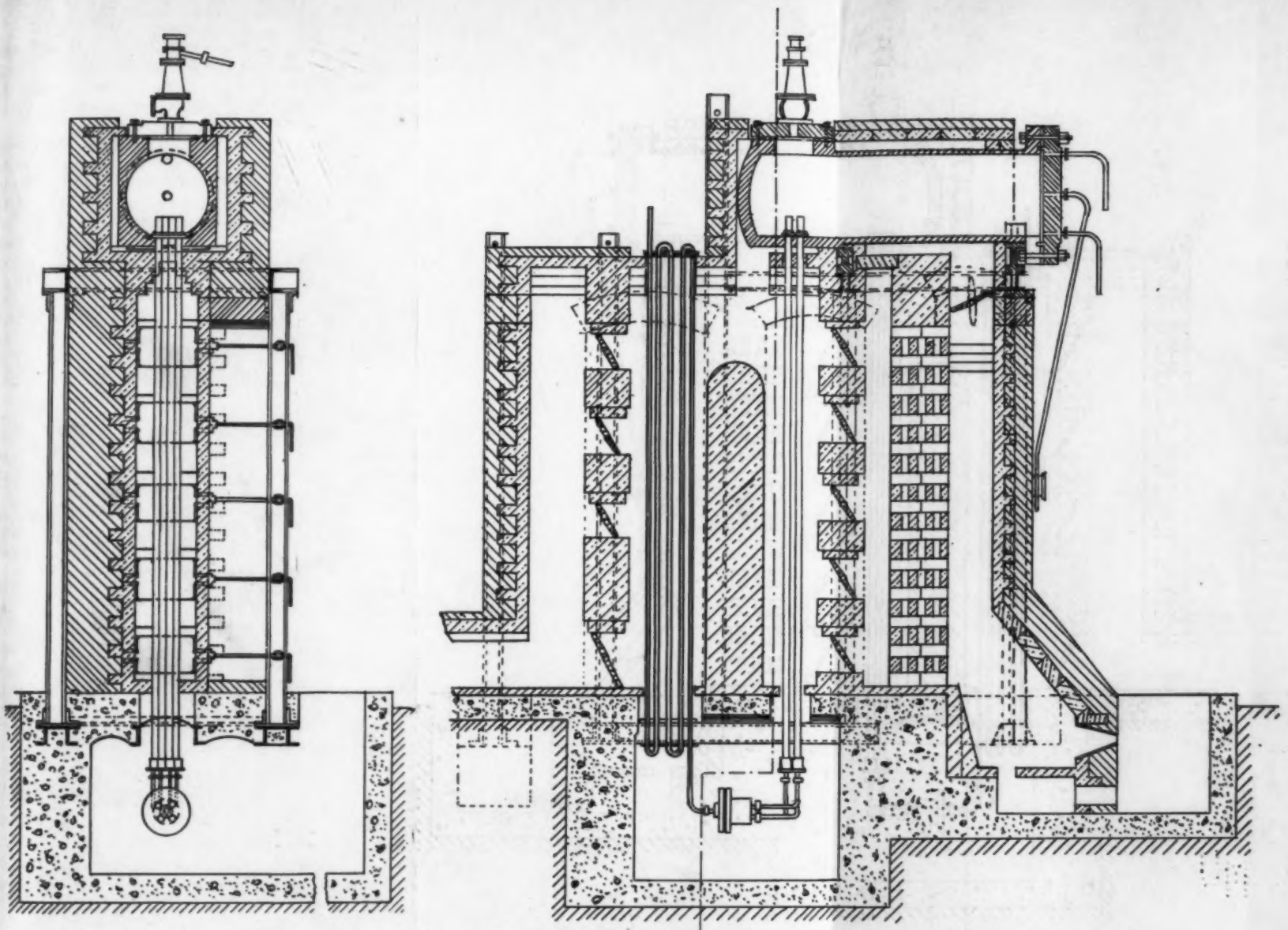
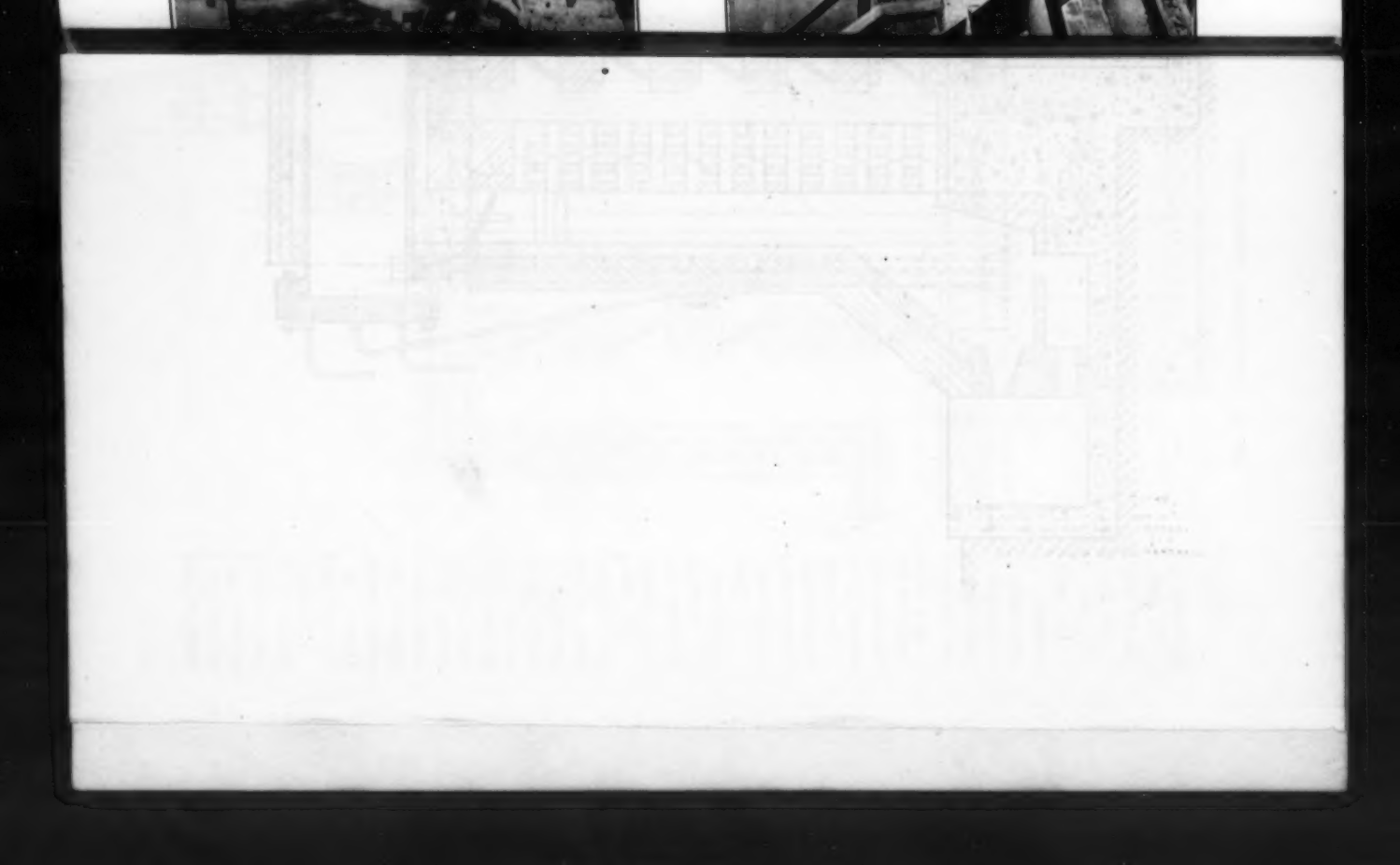


FIG. 9. AULD-DUNSTAN HERRING PLANT.



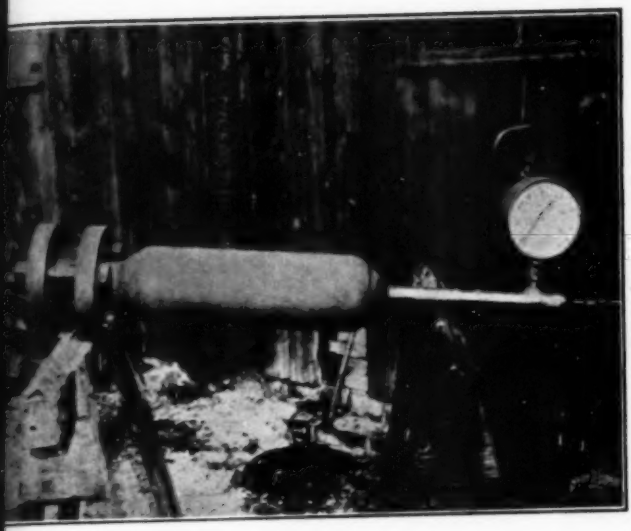


FIG. 10.

BERGIUS EXPERIMENTAL AUTOCLAVE.

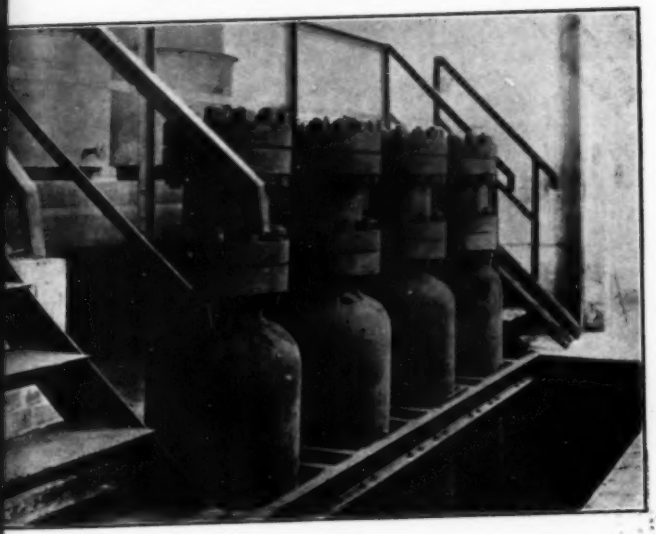


FIG. 11.

BERGIUS COMMERCIAL UNIT, SHOWING JOINTS.

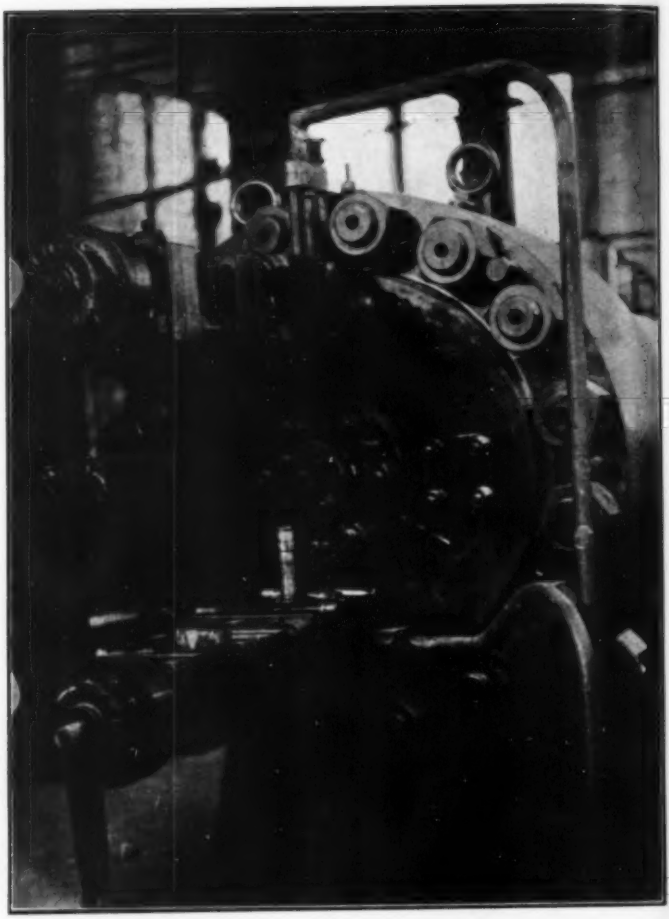


FIG. 14.

END VIEW OF REACTION CHAMBER, BERGIUS LARGE-SCALE PLANT.

for all but the lightest products; this can be attained by using pressures of the order of 25 to 30 atmospheres. This high pressure also directs molecular scission towards the middle of the molecule, thus limiting the amount of gas and carbon formed.

(2) The yield of light spirit should be deliberately restricted. This for two reasons:—

(*a*) The retention of a considerable mass of the heavier oil helps to hold up the carbon formed and to move it forward to the point most suitable for its deposition. This is especially important when cracking asphaltic residues.

(*b*) The greater the extent of decomposition the poorer the quality of light spirit or the greater the amount of gas and carbon formed. The reason for this is that the thermolytic decomposition of a paraffin hydrocarbon appears to proceed along definite lines, and, at the best, successive disruption of the paraffin molecules must increase the percentage of unsaturated compounds, or at the worst produce gas and carbon. This explains why a cracked oil is not so suitable as an uncracked one for the production of light products, and why the number of times an oil can be cracked is limited.

(3) For each oil there is a definite and fairly well defined narrow range of temperature at which appreciable decomposition occurs. Above that temperature decomposition rapidly increases.

(4) There appears to be a marked time factor, which is a function of the temperature, governing the products of light spirit. There is an appreciable lag between the moment of attaining the thermolytic temperature and the formation of the products, and the temperature must be maintained for a considerable time if the disruption is to proceed to the maximum extent corresponding to that temperature.

(5) It follows that the rate of flow of the oil must be a direct function of the temperature, and controlled correspondingly.

(6) It is impossible to prevent the formation of measurable quantities of carbon, and this difficulty must be met by inducing the deposition of carbon in places suitable for its removal. The plant must, therefore, be of the simplest type with as few bends and corners as possible where carbon can accumulate. Each part must be readily accessible for taking down or for cleaning. Local overheating, which must tend to produce highly undesirable conditions, must be avoided.

On the basis of the above principles a general procedure has been developed.

Procedure.—The thermolysis of the heavy oil is carried out in three distinct stages, which in effect are zones of temperature and

rate of flow. In the first or preheating stage the oil is carefully heated to a point, preferably not more than 25° C. below what we defined as its "Optimum temperature," which is the temperature at which the specific extent of decomposition occurs, once the molecular inertia has been overcome. In this stage the rate of flow is immaterial, and the preheater can be of any form compatible with efficient temperature control.

In the second stage the oil is quickly raised to a temperature about twenty degrees above the optimum. This stage is very important and must be carefully controlled. It is here that advantage is taken of the time lag to give the oil its impetus towards disruption without materially effecting decomposition. This portion of the plant, termed the "Thermolyser," consists of a number of pipes in parallel of such a bore that the oil can be rapidly heated throughout its bulk, and of such a length that the oil has passed through with minimum amount of actual decomposition, or, at any rate, of separation of carbon.

After leaving the thermolyser the oil passes forthwith to the "Reactor." This is a vessel of such dimensions that in passing through it the oil remains for at least the amount of time necessary to obtain equilibrium as regards the specific extent of decomposition required. By suitable means the reactor is maintained at or above optimum temperature. Owing to the endothermic nature of the reactions involved a certain amount of external heat must be supplied to do this. The position of the reactor is determined by the need of avoiding gas locks, and shape by the accessibility necessary for cleaning. Since most of the carbon is actually formed in the reactor, and since it is of considerable size and the oil in it fairly quiescent, the bulk of the carbon produced in the process is deposited here. The cracked oil is drawn from the highest point of the reactor, condensed or dephlegmated, and discharged into a gas separator.

This plant has successfully cracked kerosene, gas oil, Scottish shale oil, paraffin sweats, Persian and Mexican fuels, but like other plants it will not give a high yield of spirit from heavy residues and at the same time run for an indefinite period. The length of time it can operate is limited by the size of the reactor.

Yields of light spirit can readily be obtained varying from 10 to 30 per cent. Heavy residues which will not pass the Admiralty fuel test may be processed, producing a limited quantity of spirit and a liquid fuel which does not gel on standing for a considerable time.

The Bergius process[13] has attracted considerable attention, particularly in countries possessing much coal but little or no oil. The early work of Bergius led to the formation of artificial coal

[13] Brit. Pat. 4574 of 1914.

from cellulose, wood, etc.; these experiments were intended to reproduce the natural methods of coal formation by variations in temperature and pressure. He was successful in producing a black powder, the carbon content of which was 84 per cent. under a temperature of 349° C. and 160 atmospheres pressure. This substance possessed the properties of ordinary bituminous coal, and on further heating under pressure it passed to the anthractic type. Bergius discovered that this substance was susceptible to hydrogenation by heating to 400° C. in the presence of hydrogen for some hours, and 70 per cent. of the product was soluble in benzene. In later experiments coal was mixed with oil, and it was

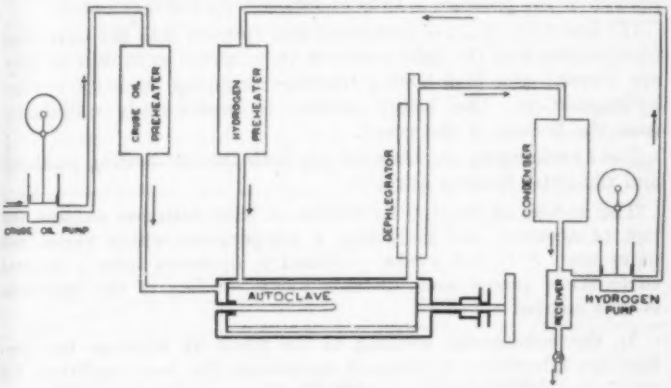


FIG. 12.

BERGIUS COMMERCIAL PLANT.

found that natural coal was converted up to a 90 per cent. yield of oil, provided that the carbon content of the coal did not exceed 85 per cent.

The products were of the consistency of thin coal-tar which yielded fractions suitable as fuel oil.

In the cracking of oil by the usual methods gas and coke are produced, the latter being a great hindrance to the continuity of working, and, further, the higher the carbon content of the raw oil the greater is the amount of coke deposited in the cracking plant, and for this reason it is not commercially possible to crack heavy asphaltic oils or residues to give a high spirit yield. Bergius took up the problem, and by applying heat in the presence of hydrogen under great pressure stated that practically no coke and

very little gas were produced when he cracked heavy oils at a temperature of about 450° C. and 100 atmospheres initial pressure.

Bergius developed a laboratory apparatus capable of withstanding very high pressures. The essential part of the plant being a simple linear joint, a double cone, making a metal to metal connection, was found to be efficient under the conditions of working.

The commercial unit differs little from the experimental plant. The apparatus employed consists of a heavy horizontal steel cylinder. Inside the cylinder there is a cast-iron vessel and between them a current of highly-heated inert gas, CO_2 or nitrogen, at the same pressure as the oil and hydrogen within the inner vessel. The greater portion of the pressure is thus maintained by the outer shell.

Oil and hydrogen are preheated and sprayed into the autoclave continuously and the light products are removed as rapidly as they are formed, the high-boiling fractions dropping back for further hydrogenation. The heavy residue is continuously withdrawn from the bottom of the vessel.

Heat exchangers are arranged for both the out-flowing products and the outer heating nitrogen.

The system of heating by means of inert nitrogen reduces the risk of accident and maintains a temperature which varies not more than 5° C. for weeks. Control is operated from a central switchboard placed some distance away. Safety of the operators is thus assured.

In the commercial working of the plant at Rheinau the preliminary laboratory experiment determines the best conditions for rapid and efficient hydrogenation. The autoclave is of 5 litres capacity and is charged with a weighed quantity of oil, hydrogen is pumped in to a definite pressure and the vessel is heated for about an hour by gas jets and rotated in a horizontal position at about 60 revolutions per minute.

The pressure increases at first, but as hydrogenation proceeds it gradually falls off and eventually becomes more or less constant, thereby differing from the ordinary cracking process, where the pressure steadily increases, even when the temperature becomes constant. The apparatus is allowed to cool, and samples of gas are withdrawn for analysis, the amount of hydrogenation being thus ascertained. The autoclave is finally opened and the contents weighed and distilled.

In the commercial unit the autoclave is thirty feet long and three feet in diameter, placed on concrete slabs sloping towards the closed end. It is fitted inside with a stirring device which penetrates to the far end. The heating is effected by passing nitrogen through

coils, heated in a furnace, then through the annular space between inner chamber and the heavy steel wall of the autoclave.

The plant can deal with fifty tons per day, and as no carbonisation occurs continuous working for an indefinite period is practicable. The hydrogenation is in most cases accompanied by very little thermal change, but on the whole the reaction is believed to be slightly endothermic. The final pressure reached is, in some cases, as high as 280 atmospheres.

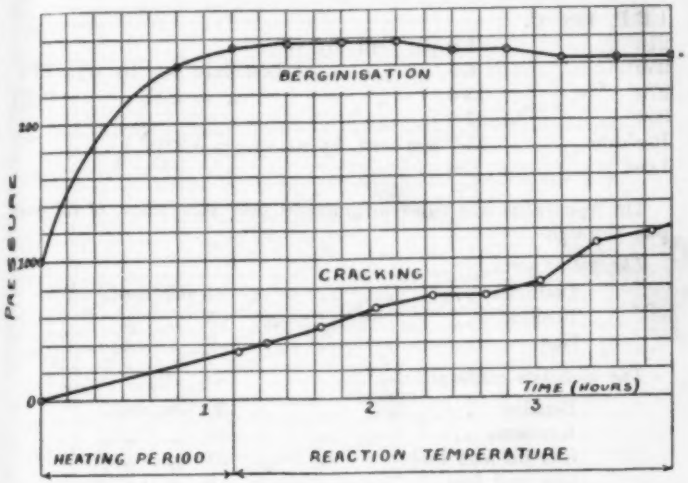


FIG. 13.

COMPARISON OF PRESSURE CURVES FOR BERGINISATION AND CRACKING.

With regard to the hydrogenation of coal the continuity of the process is brought about by grinding the coal to pass a 400 per inch mesh sieve and mixing with oil. This mixture can be circulated by pump.

Bergius claims that any coal containing less than 84 per cent. carbon, on an ash free dry basis, can be successfully hydrogenated at a temperature of about 400° C. and pressure up to 200 atmospheres, with the production of hydrocarbons similar to petroleum distillates.

The hydrogenation of coals containing more than 84 per cent of carbon has not been successful.

As an example of the work done by the Bergius plant a test made on a heavy residue may be quoted:—

The Properties of the ingoing oil were—

Specific gravity at 15° C.	0·896
Viscosity at 20° C.	0·812 Engler=237 Redwood.
Flash point	77° C.=171° F.
Hard asphalt	0·84 per cent.
Sulphur	1·02 per cent.

Engler Distillation—

I.B.P. 198° C.		
210°	1·0 per cent. by vol.	
250°	6·5 „	Distillate p.c. by wt=23·7
270°	13·0 „	„ S.G. =0·821
300°	27·5 „	
Residue	75·7 per cent. by wt sp. gr. 0·921.	
Loss	0·6.	

The apparatus was run continuously and 4650 kilos. of oil were put through.

The yields were:—

Distillate	84 per cent.
Residue	8 „ „
Gas	8 „ „

The distillate contained:—

Benzine	30 per cent.
Kerosene	25 „ „
Gas oil and fuel	37 „ „
Gas and loss	8 „ „

The hydrogen consumption was about 1 per cent. and the benzine, after refining with less than 1 per cent. acid and soda, was water white and contained 0·07 per cent. sulphur. The kerosene was slightly coloured and both benzine and kerosene had a pleasant odour. Fuel consumption was about 6·5 per cent. and the gas produced contained about as much free hydrogen as is required for the Berginisation of the oil.

Opinions differ as to Bergius's claims regarding hydrogenation of the liquid products produced by this process, and different investigators have been working on his method.

H. I. Waterman and J. N. J. Perquin[14] are investigating the Bergius process from a chemical standpoint and their results published up to date lead to interesting conclusions.

[14] *Journ. Inst. Petr. Techn.*, X., 45, p. 670, Sept., 1924.

They remark on the complexity of the subject and complain of the difficulty in comparing the unsaturation of products, the iodine and bromine values being vitiated by substitution effects.

Experiments on a fraction of Borneo oil and on Mexican asphalt at various temperatures and pressures with and without hydrogen

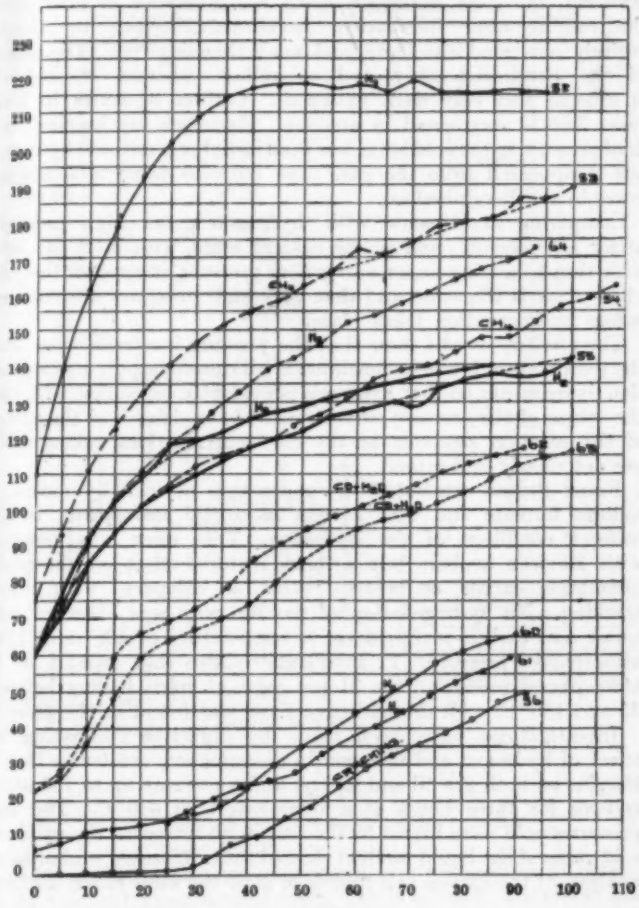


FIG. 15.

CURVES ILLUSTRATING WATERMAN'S EXPERIMENTS.

show no definite advantage in hydrogenation, although hydrogen disappears as shown by the falling pressure curve and the residues show a lower specific gravity than those of cracked products. For Borneo oil 403 to 410° C., for Mexican asphalt 385 to 390° proved to be the best temperatures.

The results of Berginisation do not differ greatly from those of cracking, the chief difference being the difference of gravity in the residue after distillation. Solid paraffin can be almost entirely converted into liquid and gas if time is given. The colour of the Berginised oil is red or yellow, whereas cracked oil is opaque and very dark in colour. Carbon separates in both cases, but is very small in amount. Hydrogen is absorbed, the final pressure in the cold being less than initial pressure and hydrogen has disappeared from the gas. The bromine value is somewhat lower in the Berginised oil.

Comparing experiments with, hydrogen under high pressure, under low pressure, and in the nascent state, with inert gas, and with simple heating under autogenous pressure, it appears that the yield of oil is the same, and that very high pressures are required before hydrogenation takes place.

The pressure curves show that the pressure increases, even after the temperature becomes constant, in all cases except in hydrogenation experiments, so that hydrogen is evidently consumed, although the course of the pressure curves cannot be explained, as the nature of the reaction products or the chemical reactions taking place are not clearly understood.

Franz Fisher attributes[15] hydrogenation of coal, by means of sodium formate and with carbon monoxide and steam, to the nascent condition of the hydrogen. This work was repeated with Mexican asphalt, but without material effect on the yield, distillation curves, or bromine value, as compared with simple cracking. No hydrogenation of paraffin wax was observed with water and carbon monoxide at a temperature of 420° and 113·5 atmospheres pressure. P. Bruylants[16] states that asphalt at 50 atmospheres pressure gave 31 per cent. of spirit boiling between 35 and 150° C. All the hydrogen fixed was found in the gases.

Investigations have been made by ourselves comparing the effect of hydrogen and nitrogen in an autoclave similar to that of Bergius on both gas oil and fuel oil under pressure up to 135 atmospheres for three hours at a temperature of 410° C. The final pressures cold were higher in the tests with nitrogen, the sulphuric acid value of the liquid product showed little difference, and ultimate analysis of the carbon and hydrogen gave the same result for both.

[15] *Ibid.*, VIII., 30, p. 116, Jan., 1922.
[16] *Bull. Soc. Chim. Belge*, 1923, **32**, 194-214, and *J.S.C.I.*, 1923, **42**, 700A.

The analysis of the gas showed very low unsaturated content, in the neighbourhood of 1 per cent., in both cases. The specific gravity of the residue after distilling to 200° C. was generally slightly

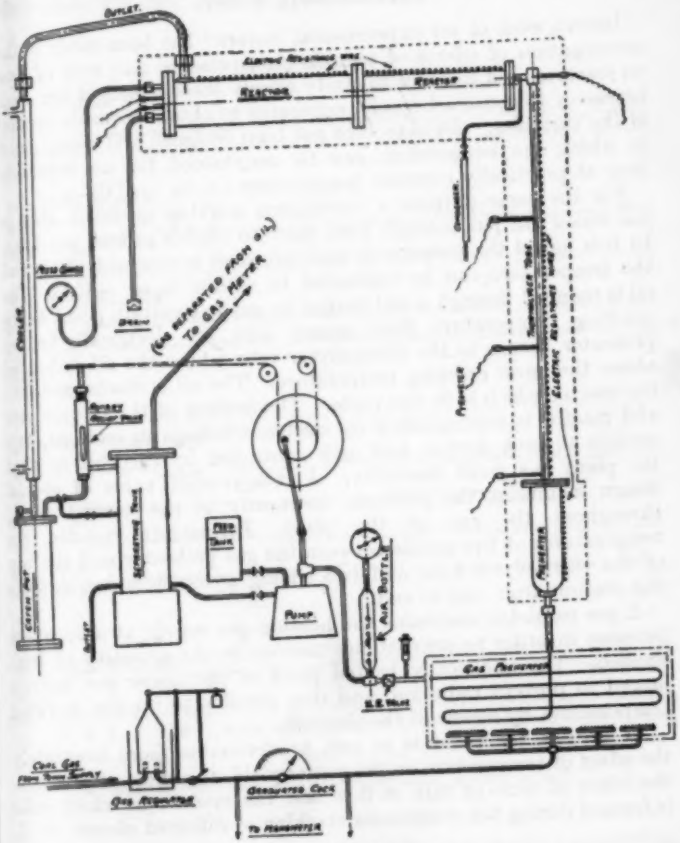


FIG. 16.

DIAGRAM OF ANGLO-PERSIAN MODEL PLANT.

lower in the hydrogenation experiments but not sufficiently definite as to rule out experimental error. It is evident, therefore, that hydrogenation of the liquid products is not definitely proved for pressures under 150 atmospheres, but it is possible that hydrogena-

tion takes place at much higher pressures as indicated in Waterman's experiment where the pressure curve becomes horizontal about 280 atmospheres.

Experimental Plant.

Recent work of an experimental nature[17] has been made in the investigation of effects of temperature, pressure and rate of flow on cracking, and in order to study closely these effects it has been necessary to construct special apparatus to obtain accurate control of the variables. An autoclave has been designed and constructed in which the temperature can be maintained for an indefinite time at practically constant temperature (+ or − ¼° C).

For the same purpose a continuous working model is also in use which can put through from three to twelve gallons per hour. In this model the pressure is maintained at a constant point and the temperature can be controlled to within + or − 1° C. The oil is pumped through a coil heated by gas to a certain point below cracking temperature, then passes into an electrically-heated preheater, thence to the thermolyser tube where the oil is heated above the mean cracking temperature. The oil is discharged into the reactor which is in two parts. The heating of the thermolyser and reactor is accomplished by electric windings in sections, two circuits to each section and each controlled by rheostat so that the plant has great flexibility. A rotary relief valve of special design maintains the pressure, constantly at the desired point, throughout the run of the plant. Pyrometers register the temperatures at five points between the gas preheater and the top of the thermolyser tube and two sliding pyrometers can explore the reactors from end to end.

A gas regulator maintains the heating gas supply at a constant pressure in order to prevent fluctuations in the quantity of heat applied. The electrically heated parts of the plant are heavily lagged to prevent radiation and it is possible to set the working temperatures by means of the rheostats.

At present the plant is in use, to determine more accurately the effect of temperature on the petrol yield, the effect of pressure, the effect of time or rate of flow and the manner in which coke is formed during the continuous cracking of different classes of oil.

The Refining of Cracked Products.

The difference between straight run spirit and the product from cracking processes entails a different method of refining, and in order to find a suitable economical process there has been a considerable amount of investigation during the last few years.

[17] Anglo-Persian Research Laboratories.

The nature of cracked spirit varies, on account of the varying composition of the raw materials and the different conditions under which it is formed. The conditions appear to have more effect than the raw material, and there is one outstanding fact

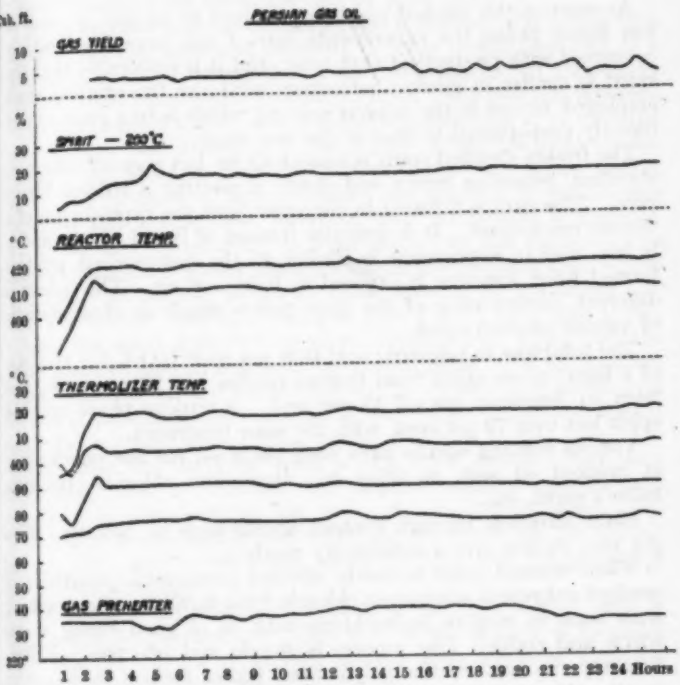

PERSIAN GAS OIL
GAS YIELD
SPIRIT — 200°C
REACTOR TEMP.
THERMOLIZER TEMP.
GAS PREHEATER
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 Hours

FIG. 17.

TEMPERATURE CURVES, ANGLO-PERSIAN MODEL PLANT.

which is impressive and that is, the difference in the composition of the products obtained by vapour phase and liquid phase processes.

In vapour phase cracking, usually carried out under atmospheric pressure, the product is highly unsaturated and contains compounds which render it more difficult to refine with ordinary refining agents.

Much of the earlier work, of course, was concerned with vapour phase spirit. Such spirit is very poor in quality and deposits

large amounts of gum on standing. Refining methods for this spirit must be drastic; losses are great, and the final products are, as a rule, of inferior quality. The treatment of liquid phase cracked spirit is more simple and numerous methods have been devised which result in the production of water white gasoline of inoffensive smell.

As most of the cracked gasoline produced at present is more or less liquid phase, the experiments carried out have been mainly concerned with products of that type; and it is noticeable that the spirit is similar in general behaviour, whatever the original stock employed, except in the sulphur content, which is to a great extent directly proportional to that of the raw stock.

The freshly distilled spirit is almost white, but goes off colour on standing, becoming brown and slowly depositing a reddish-brown gum. This gum is different in character from the typical gum of a vapour cracked oil. It is granular instead of liquid, the quantity is less, and in appearance is similar to the polymerised product formed when kerosene is exposed to light and air. The colour is different, having none of the light yellow shade so characteristic of vapour cracked spirit.

The total loss to sulphuric acid (100 per cent. C.O.V.) in the case of a liquid phase spirit from Persian residue was 22 per cent., and from an American gas oil 25 per cent. A vapour phase cracked spirit lost over 70 per cent. with the same treatment.

Various refining agents have been proposed for the purification of cracked oil such as silica gel, aluminium chloride, bauxite, fuller's earth, etc.

Plain filtration through contact agents such as bauxite, silica gel, etc., do not give a satisfactory result.

When cracked spirit is slowly distilled over small quantities of crushed anhydrous aluminium chloride[18] the distillate, after washing with soda to remove hydrochloric acid, is of good smell, water white and stable. The process is simple and effective. Unfortunately the non-volatile polymerised bodies formed in quantity in the still are very resinous and deposit on the walls as a sticky mass difficult to remove and involving loss of aluminium chloride. So far these inherent difficulties have not been overcome. Recovery of aluminium chloride is also difficult (compare the cracking processes involving its use), and the operation therefore likely to be expensive.

The use of anhydrous zinc chloride for refining cracked spirits has also been patented, and its action is similar to aluminium chloride, much less drastic, but the problem of refluxing or distilling over this solid is the same.

[18] Sunstar, Brit. Pat. 119,751.

A modification of this process[19] wherein the zinc chloride was mixed with an equal quantity of zinc dust showed a limited saturation effect and considerable mechanical advantage, for the mixture remained dry and could be handled with an ease impossible with the zinc chloride alone. Polymerisation is slower and more even. The distillates were colourless and of good smell.

When cracked spirit at ordinary room temperature is mixed with bauxite, floridin, activated charcoal, or other porous materials of a similar nature,[20] polymerisation of the most unsaturated compounds present takes place with evolution of heat. The reaction proceeds more vigorously if the contact material is maintained at an elevated temperature, and if kept at a few degrees above the final boiling point of the liquid, so that the reaction takes place in the vapour phase, the products of polymerisation are retained in the contact material and a colourless, sweet-smelling condensate is obtained which has lost its tendency to form gums. In this operation the contact material becomes clogged with the polymerised gum, which is difficult to remove and may cause choking of the filters. It has been found[21] that by working at about 100°C., and thus maintaining the spirit substantially in the liquid phase, polymerisation takes place equally as well as in the vapour phase. The polymerised products, however, are washed out by the oncoming material, and by this means the contact material is kept clean and free to continue work for a longer period than would otherwise be the case. On issuing from the filters the spirit is of a much darker colour than originally, since it contains the original volatile gum-forming constituents dissolved in the form of non-volatile gums. By means of a simple distillation, therefore, the latter are left behind in the still, and a colourless, sweet-smelling and non-gumming product is obtained.

The contact material can be steamed out and roasted, and is then ready for further use. This part of the process is identical with that in use for recovering bauxite after kerosene filtration and presents no difficulties.

The result of the treatment is to lower the amount boiling below 100° C. by about 2 per cent., as compared with the untreated material, but otherwise the boiling points are identical. The sulphur content is reduced from about 0·3 per cent. to about 0·15 per cent., but the product remains quite stable in bright sunlight for many months without gum formation or reversion in colour. A sample made from a vapour phase gasoline has already successfully withstood twelve months' exposure in a window with a south aspect.

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[19] Anglo-Persian Research Laboratories.
[20] Brit. Pat. 109,077. *Ind. and Eng. Chem.*, **16**, 913. (Hall) (Gray).
[21] Remfry, Brit. Pat. 212,500 of 1924.

Cracked spirits treated with strong sulphuric acid give acid tars in quantity varying with the unsaturation of the spirit and the amount and concentration of the acid used. The spirit undergoes loss both by actual removal of unsaturated and polymerisable bodies and by the raising of its boiling point by polymerisation of some of the compounds present. The residual spirit can be obtained water white and non-gumming and with a lower sulphur content. The smell is altered and is peculiarly terpenic in character. The ordinary American practice is to use 1 per cent. or 2 per cent. of C.O.V., but with bad cracked products as much as 4 per cent. or 5 per cent. is sometimes needed to give the desired results. The losses are then proportionately greater and the peculiar smell of the spirit more marked.

During the acid treatment alkyl sulphates are apparently formed, and these cannot be removed by soda washing, and, if left in, may cause the subsequent reversion of the spirit. They must be removed by distillation, but during distillation they generally decompose and sulphur dioxide is formed.

The effect of different proportions of acid have been investigated and samples have been treated with ½ per cent., 1 per cent. and 2 per cent. of acid.

The sulphur content was reduced in direct proportion to the amount of acid used, the original being ·102, ½ per cent. ·06, 1 per cent. ·04, 2 per cent ·02. Sulphur dioxide is formed in the redistillation of the treated spirit, and the greater the treatment the greater the amount of SO_2 evolved. This effect takes place about 130° to 140° C. and is accompanied by darkening of the liquid due to the separation of a finely divided carbonaceous solid.

A combined treatment with acid and bauxite has been investigated and petrol obtained by methods involving a hot bauxite treatment, 1 per cent. acid and soda; bauxite filtration and redistillation has good stability showing no signs of reversion, and the smell is more like straight run spirit than any hitherto handled.

Of all the methods tried the sulphuric acid and soda, redistillation, and a final soda wash is probably the most economical.

Another method of treating cracked products has been patented by R. H. Brownlee,[22] whereby oil of high flash point, high viscosity and low cold test is obtained by polymerisation of a light unsaturated oil, such as gas oil from synthetic crude, by agitating it with a catalyst at 200° to 400° F. ($AlCl_3$ HCl, or a halide, or reagents which will produce a halide, in its vapour state.)

The light hydrocarbon is purified by treatment with sulphuric acid then acted on by the catalyst in a vessel provided with an agitator and a heating coil. In about 1½ hours the action is com-

[22] U.S. Pat. 1,309,432 of 1919 and Brit. Pat. 141,753 of 1921.

plete, the sludge is allowed to settle off. The oil is cooled, soda treated to precipitate colouring matter and washed with water, then distilled with the aid of steam.

The distillate includes products having the flash points of naphtha and kerosene and a number of lubricating oils which have a very low cold test.

DISCUSSION.

The President thought the members were much indebted to the authors for their very interesting paper. The Institution as a whole was under a debt of gratitude to Dr. Dunstan for the way in which he placed before it, as embodied in several papers submitted to the Institution, the results of his various researches. He hoped the paper would lead to an important discussion; at any rate he had no doubt the chemists present would have something to say on the last curves which had been shown.

Dr. W. R. Ormandy in opening the discussion, said the statement was made in the paper that oil was cracked and a spirit was obtained, which could be used for motor purposes, that spirit being compared with spirits which motor users had hitherto been accustomed to use, namely, straight run spirits. The statement was further made that the spirit contained so much unsaturated material, but that it was capble of being used when it had been adequately refined. Before, however, any comparison could be made in regard to any spirits it was essential that information should be available in regard to the methods of testing employed, and the whole of the results from the point of view of a comparison of cracked spirits, which were bound to be produced in large quantities, with the older motor spirits were inexplicable unless the conditions under which they were tested were defined. For instance, it was said that with a cracked spirit produced by the A process, as compared with the B process, the unsaturateds amounted in one case to 10 per cent. and in the other to 20 per cent. But how were the unsaturated contents estimated? Were they determined by a bromine number, by permanganate or by washing out with sulphuric acid; what strength of sulphuric acid was used, and at what temperature, and what quantities were employed? Those were a few of the variables that might occur, He knew of one case in which spirit cracked by one of the processes described in the paper could be used with safety in the crude state as it came straight from the distillation plant. It was being used to the extent of many hundreds of gallons per day by a fleet of 25 vehicles, and although it contained anything from 10 to 25 per cent. of unsaturated bodies, according to the process used to determine the quantities, the vehicles were running perfectly well. On

the other hand, many chemists would say that a cracked oil which contained a very high percentage of unsaturated, was an absolutely impossible article to use. The time had now arrived when spirits would be used, which were either wholly cracked or largely cracked, and it was necessary for the Institution to think about defining new means of analytical determination, which would enable it to say what was a good spirit and what was a bad spirit and how to compare one with another. The old methods of testing, which were applicable to straight run spirits were not applicable to cracked spirits, and if they were relied upon a large amount of material might be rejected, which was admirable for the purpose for which it was employed. He thought it would be of great value to all chemists if the authors could state in a short addition to the paper the analytical methods employed. It might be thought that he was raising rather a side issue, but personally he thought it was a matter which would be of very great importance to the industry as a whole, because the question was going to arise to what extent any type of cracked spirit was suitable for motor car use. A man who possessed an expensive motor car did not want to make experiments with the spirit he used for driving it; he would wait for those who were experts in the industry to tell him whether a particular spirit was a suitable one or not, and it was, therefore, necessary to devise means for determining suitability. It was well known that a straight run spirit, if evaporated in the copper dist test might only give two or three milligrammes of residue, but a cracked spirit might give very much more, depending on the degree and the type of refining used. But he knew of plenty of cracked spirits which might be used with perfect safety in a motor car, spirit which contained 10, 20 and 40 times as much residue as would be found in straight run spirit, and yet the ordinary chemist would condemn that spirit on the ground that it gave far too great a residue in the test. The value of a spirit at the present time was not based entirely on its heat of combustion and latent heat, but on its ability to stand a high compression. There were thousands of motor cars on the road that could not run with some spirits and yet could run with others, because some spirits had a higher compression value. A cracked spirit had a much higher toluol number than the paraffin compound from which it was frequently made, and it was greatly to the advantage of the industry that cracked spirit should be used, because, taking the world's production of motor spirit as a whole, there was more spirit which would only stand a low compression than the quantity that would stand a high compression. In the next place, he desired to mention that the authors had paid a very grateful tribute to the preliminary work of Bergius on a line of research, which he had made particularly his own, namely, that of cracking and hydrogenating

simultaneously. He did not think he would be giving any secrets away when he stated that modern cracking processes, using high pressures, gave such good products that the question of carrying out the operation under the Bergius conditions, in so far as it related to oil might, he thought, be disregarded as a practical proposition, except in special cases. But he desired to take issue on the point raised by the authors as to whether hydrogenation did take place or not. He found it was a fact, from certain products which had been hydrogenated and sent to him for examination, that the petrol fraction of a cracked, hydrogenised or Berginised oil, when shaken out with 80 per cent. sulphuric acid with the object of removing the unsaturated resulted in a loss of 1·3 per cent., and also the aniline point was sent down about 1·3°, comparing the aniline point of the product before and after shaking out with 80 per cent. sulphuric acid, *i.e.*, the two methods generally speaking confirmed each other, that the unsaturated were exceedingly low. An estimation of the aromatics and the naphthenes by the method suggested by Dr. Dunstan and Dr. Thole and Marshall, *i.e.*, by washing out with acids of various strengths and by means of the aniline point, showed that the product had 58 per cent. of aromatics and hydro-aromatics, 10 per cent. of paraffins, 1·3 of unsaturated and the rest naphthenes. No cracking process that he had ever heard of in which hydrogenation did not take place at the same time could give a product like that. He thought the mere estimation of the carbon hydrogen ratio was not so significant in its indication as a determination of the physical properties of the liquid that was produced. Another aspect of the subject upon which he wished to touch, which he thought was much more important than the hydrogenation of oil (because he did not think that was a generally feasible proposition in face of the very admirable straight cracking processes in the liquid phase, which were now available) was the conversion of coal into oil. Since the information which Dr. Dunstan had obtained a good deal of work had been done; and whatever doubts might have existed as to the absorption of hydrogen in the treatment of oil by the Bergius process under pressure there was no doubt in regard to the fact in the treatment of coal, because the amount of hydrogen absorbed in a plant treating 20 kilogrammes of coal per hour varied from 3½ to 5½ per cent. of the weight of the coal. It was very interesting to note that the reaction was exothermic and that the amount of heat evolved was found to be practically that which one would reckon to be evolved, assuming that a given medium type of hydrogenation compound was formed; in other words, that the exothermic nature was of the order which a chemist would expect it to be. The authors had stated that the products produced should be carefully investigated, and that was undoubtedly correct. Practically nothing was known

about them, very largely owing to the fact that raw materials had not been available; but he was glad to say that drawback did not now exist and that it would be possible to commence to find out the types of bodies which were produced. From a ton of average slack containing 10 per cent. of ash and 5 per cent. of water, it was possible to get 50 per cent. to 60 per cent. of the weight of the coal in the form of oil, and of the coal substance itself less than 10 per cent. was left unchanged. Of the total oil produced approximately 30 per cent. would consist of motor spirit, 35 per cent. Diesel engine oil and 35 per cent. of a pitch, which had extraordinary properties and with which it was impossible yet to say what could be done. That hydrogenation took place in coal was certain. He desired, in conclusion, to refer to the group of experiments carried out by Dr. Bergius dealing with the question of the hydrogen absorption of oils. Dr. Bergius pumped various types of oils through steel tubes, which were heated in a metal bath to varying temperatures. The pressure could also be varied, and the temperature increased at a given pressure until the first evidence of the formation of carbon became noticeable. Under those conditions, by slightly increasing the temperature the production of carbon could be very rapidly increased, and when at this slightly increased temperature nitrogen was pumped in the carbon product continued just as though the nitrogen were not there. If hydrogen were pumped in under those conditions then the temperature could be raised a good many degrees and still no carbon would be produced. That was a positive means of proving that under a given set of conditions, relationship between pressure, temperature and velocity of flow, carbon would be deposited with a given oil in the absence of hydrogen and not in the presence of hydrogen. That again was, he thought, a more positive proof than a mere estimation of the carbon hydrogen ratio.

Dr. Victor Henny said he hoped the members would bear with him if he ventured to make a few remarks on the subject of commercial cracking. A few years ago he was sent to the United States by a very large European Oil Company to investigate cracking. Most of the many processes which he then investigated had been mentioned by the authors in the course of their paper. The vapour-phase process at Detroit was also demonstrated to him. The commercial plant at Tulsa mentioned by the authors constructed in 1922 had never been a success; and in 1923 the Company which had that commercial plant at Tulsa chose a different cracking process. The Company with whom he was working during that time actually constructed one of the plants with a vertical still, also one using high pressures, and also tried the super-pressure process. Finally, in all the new refineries of this concern, the

Dubbs process had been adopted as a general rule because of its flexibility and its possibilities of cracking fuel oil direct. With regard to the question of recycling mentioned by the authors, he did not think that generally speaking refiners attached enough importance to the remark made on page 743. "This explains why a cracked oil is not so suitable as an uncracked one for the production of light products, and why the number of times an oil can be cracked is limited." Theoretically he believed that all oils could be converted finally into motor spirit, gas, coke, and loss; but to compare properly the cracking processes the only reasonable method was to compare the yield in one passage through the apparatus. With regard to the cracking of kerosene, the petrol obtained from the cracking of kerosene had as a rule a higher specific gravity, 0·770 as against 0·755. That was mainly due to the fact that at the present time in kerosene there was a fraction of about 30 per cent. to 50 per cent. boiling below 250° C. That fraction was merely a heavy naphtha, which was not decomposed in any of the cracking processes, except possibly when using superpressure. If they topped off the fraction of kerosene boiling below 225° and cracked the bottoms of the kerosene, a motor spirit or a petrol would be obtained from the bottoms of the kerosene, which had the low gravity of 0·755. If that 0·755 spirit was mixed with the heavy naphtha a mixture would be obtained, having about 0·770 specific gravity, and having about the same characteristics as if the whole kerosene was cracked. The losses in refining were no longer very great; they did not exceed about 4 per cent. in properly operated refineries. As Dr. Ormandy had said, it was generally recognised that cracked motor spirit was not so inferior as had been supposed; especially as unsaturated spirit could stand a higher compression. In the refining in America the product was steam-distilled afterwards, because it was found that after any acid treatment with any cracked oil it was necessary to use steam-distillation if the petrols were to remain water-white. Dr. Ormandy had said that the unsaturated spirit must not be considered as an inferior motor spirit. In 1923 the total amount of cracked gasoline produced in the United States, according to a statement by the Standard Oil Company of Indiana, was one billion 850 million gallons, so that there were many people who considered cracked spirit pretty good. The amount of cracked gasoline represented 21 per cent. of the total amount of gasoline produced in the States; and it was expected that in 1924 about 25 per cent. of the total amount would be cracked spirit. It was evident, therefore, that there was a big future for cracking, and that cracking had come to stay.

Dr. F. Mollwo Perkin said he had been rather surprised to find that no mention was made in the paper of a patent taken out

by himself and Mr. Fenchell in 1913 and 1914 in which pressure was used. So far as he had been able to ascertain, no one had used pressure until he and his colleague did so. They used a pressure of something like 1000 lbs. per square inch, and a petrol, which had no gum, was produced in 1915 from heavy crude oil. He produced a bottle with the original label on it, containing the spirit which was produced on that plant. It had not been purified or rectified in any respect after it was taken off the plant. He also produced a sample, which was given to him at the same time by Mr. Noad, and the gum formation was very noticeable. It was of approximately the same date, August, 1915. The original process at which he worked was introduced in the first place by Mr. Raynard, a Belgian. He (Dr. Perkin) went over to Paris and worked the process for him, and in so doing introduced certain alterations in the plant, which made all the difference. He produced a sample made in Paris in December, 1913, which showed a certain amount of gumming. After the alterations to which he had referred were made, no gumming at all occurred when working at high pressure and a temperature of about 550 to 600° C. The oil when passed through the apparatus for condensation before the pressure was released was practically at a cherry-red heat. The oil was under such a pressure that no vaporisation took place. He had been very glad to note the authors' statement that practically all the processes which were now successfully employed worked under pressure. He produced another specimen which required a little refining, produced by Mr. Lucas's plant at the same date. It would be observed that there was a certain amount of gumming, but there was no gumming at all when they worked at 1000 lbs. pressure. No refining at all had been done in any of these cases. The material was topped, passed through a dephlegmator, and taken off. The plant broke down and work was not further carried on, due to the fact that he was at that time interested in the Ministry of Munitions, and Lord Moulton asked him whether he could produce benzol and toluol on his plant. He put through some green oil, but carbonisation resulted, the tubes being absolutely blocked. Great trouble was experienced with the joints in working under very high pressure, but this difficulty was finally surmounted. It appeared that the present American processes were worked on similar lines, but they had altered their plant so as to work at lower pressures; whether it was an advantage he was unable to say. In his own plant there was an expansion chamber, and if there was any carbon deposited it occurred there. Another improvement was before passing the material into the expansion chamber the oil was passed through tubes in a tubular boiler, and after the process was once started a a constant head of steam of 60 lbs. was easily kept. The oil was expanded in the chamber, and went straight into the dephlegmator,

the condensation products then being obtained. The residue of heavy oil was passed back through the retort. The exact loss on the gas was put down as about 10 per cent. Unfortunately there was no one behind them financially, and further tests were not carried out. It was of interest, however, from an historical point of view that that oil was produced in 1915, and had it not been for the exigencies of war he had no doubt that further experiments would have been made. He had been most interested in the résumé which the authors had drawn up of all the processes that had recently been used.

Mr. E. Lawson Lomax said he had not intended to take part in the discussion, but the paper was of particular interest to him because his first experience in regard to cracking took place as long ago as 1910. There were one or two points on which he desired to join issue with the authors, the first being in regard to pressure cracking. He had recently been doing some experiments on cracking, and had come to the conclusion that the oil was not always in a liquid phase, and that undoubtedly better results were obtained with a combination of the liquid and gaseous phase so far as the yield of light boiling hydrocarbons was concerned. To a certain extent he agreed with the authors that the further cracking was continued the more unsaturated were the light hydrocarbons that were produced. Taking mazout and cracking it under pressure he obtained a yield of 19 per cent. of low boiling hydrocarbons, which on distillation were practically water white, and simply washing them with caustic soda rendered them perfectly water white. After that treatment, by Dr. Ormandy's method of testing, namely, shaking with 80 per cent. sulphuric acid, a loss of 6 per cent. was obtained, while about 12 per cent. by weight of aromatic hydrocarbons were present, the specific gravity of the spirit, boiling up to 200°, being about 0·755. That was cracked under the combination process, partly vapour and partly liquid phase. In those particular experiments the amount of carbon in the residual heavy oil was carefully determined, and it was found there was a total of free carbon of 0·001 per cent., and in the cracking vessel there was 0·05 per cent. of the weight of the oil as carbon. In the processes for cracking purely in the vapour phase, the amount of unsaturated hydrocarbons in the spirit produced depended to a great extent on the process adopted with regard to the ratio between the diolefine type and the olefine type. It was possible to reduce the diolefines to a fairly low proportion and still have in the spirit olefines which were quite useful from a power standpoint, because they did not have any deleterious effects so far as gumming was concerned. Dr. Mollwo Perkin had mentioned the Lucas process, and had showed samples that had been standing for some time. He was afraid that particular

spirit was not refined by modern methods. He knew the history of that spirit, and it was totally unrefined, which, of course, accounted for the tendency to polymerisation.

He had been carrying out a certain number of cracking experiments with oils from such widely varying sources as producer tar, lignites, shales, and petroleums; and in every case, using the same type of plant and working under identical conditions, while it could not be said that the cracked products were identically the same, to all appearances they were exactly the same so far as physical tests were concerned. That showed, he thought, that there must be a complete dissociation of the molecules in cracking and not simply a scission as was claimed in some cases. That applied only to cracking in the vapour phase and not in the vapour and liquid phase. He thought the Institution was much indebted to the authors for a further résumé of the later work which had been done on the subject discussed in the paper.

Mr. E. H. Cunningham Craig said, that if a mere geologist who was, of course, a child in these matters, might be allowed to speak, he would like to say a few words. He had read the paper with a very great deal of pleasure, but with some little difficulty. There was one aspect in regard to which the authors had made an entirely new departure. The title of the paper was, "Recent Developments in the Art of Cracking." Personally he had always thought that cracking was a chemical process, but the members were now informed that it was an Art, and would henceforth have to regard Dr. Bergius, Dr. Dunstan and many of those who had spoken that evening as artists. It might even be possible to write a new verse for Kipling's poem, "The Conundrums of the Workshops," on the subject of Cracking, ending as follows:—

> "The devil whispered behind the still
> It's clever, but is it art?"

There were one or two questions he would like to ask. The authors seemed to suggest in the paper that there was very little hydrogenation at all going on in Dr. Bergius's process; in fact that the same results were given with nitrogen as with hydrogen. The authors also mentioned that there did not seem to be much heat effect of the endothermic or the exothermic kind. Personally he could not understand that, being sure that when coal was treated by Dr. Bergius's process the reaction was exothermic, or it ought to be; and he was inclined to think that if oil was really hydrogenated the reaction ought also to be exothermic. He would like to hear what the authors had to say in reply to that question. Speaking not as a chemist, but simply from the point of view of general principles, he would be inclined to think that the lower the

temperature and the higher the pressure at which such actions took place the better the result in the quality of oils produced, but he was open to correction on that point.

Dr. F. B. Thole said he desired to add a word of appreciation for the authors' present paper, which was in the nature of a sequel which brought up to date a previous paper on the subject. The most noticeable change during the past decade was undoubtedly the displacement of the vapour phase processes by the liquid phase processes, which could be applied to a wider range of raw materials and which gave better quality products with less loss. The fact that cracking from the commercial standpoint had been dealt with more as an engineering problem than a chemical one had led, he thought, to the overlooking of a number of chemical points, which were of very vital importance to the art. For example, the statement had been made by practically every speaker on the present occasion and by practically every person who discussed cracking, that when oil cracked it produced, among other things, coke. That statement in itself was not strictly true. The coke, which was the inevitable end product from a normal cracking process, was in itself a secondary product, the parent material of that coke, which could be isolated if the process was carefully regulated and stopped at the right point, being a viscous tarry material, not soluble in the oil which was being treated, and that viscous tar had a certain definitely localised decomposition temperature. If the temperature could be maintained just below that point, it was possible to isolate this black tar in quantity, no coke as such being obtained. If the tar was heated to a certain decomposition point it intumesced and formed a large volume of gas porous coke. The formation and separation of that tar seemed to be a point worthy of further study, because possibly a separation in the liquid condition before it became further decomposed into solid carbon might solve a good many of the coking troubles which constituted a difficulty in all modern cracking processes. Again, a more detailed study of the velocity of reactions at a close series of temperatures in the cracking range 400 to 450° might enable better results to be produced than were obtainable in the present somewhat rough-and-ready methods of temperature control. The study in such minute detail of the cracking of oils was, of course, a difficult process. Practically all the cracking which had been done had been carried out in steel vessels, but recently he had an opportunity of witnessing some experiments in which the oil was heated out under normal cracking conditions, at about 400 to 500 lbs. pressure and 400 to 450° C., the oil being enclosed over mercury in transparent silica tubes. Under those conditions the various stages in the cracking could be observed.

Dr. A. E. Dunstan, in reply, said he thought he could say that the authors agreed almost entirely with Dr. Ormandy's remarks. The estimation of the unsaturated content was a very difficult problem. The authors always followed the A.S.T.M. procedure in that case because the same method was used generally and a comparable way of assessing results was obtained. The matter was under the consideration of most oil laboratories and would have to be settled sooner or latter by the Institution's Standardisation Committee. With regard to the presence of olefines in cracked spirit and *vis a vis* their fuel value, he did not think anybody could have any objection to burning olefines at all, because it was obviously the diolefines which were concerned with the formation of gum. Dr. Ormandy spoke, of course, in a very authoritative way in regard to the work of Bergius. He would only say, so far as the authors were concerned, that their experiments were conducted under conditions which possibly would be rejected by Bergius, *i.e.*, at lower pressures than he made use of. But he thought they could say that up to 150 atmospheres, and taking the carbon-hydrogen ratio with extreme exactitude, there was no difference at all, whether nitrogen, carbon dioxide, or hydrogen were used, and, moreover, the yield of products estimated in the ordinary way seemed to indicate that the presence of any of these three gases brought about identical results. Dr. Ormandy had also referred to an oil which contained 50 per cent. aromatic hydrocarbons, although processed at a comparatively low temperature. It was well-known that in ordinary vapour phase cracking, working up to 700° C., a cracked spirit could be obtained, which contained a very high percentage of aromatics. His colleagues and he had shown that to be the case in the previous paper they had presented to the Institution. Quite recently in some experimental work they actually came across a corresponding case to that quoted by Dr. Ormandy, in which a kerosene oil was cracked and gave a 54 per cent. content of benzol, toluol and xylol at a temperature of the order of 400° C. So far as the conversion of coal into oil was concerned, Dr. Ormandy probably remembered the interesting line indicated by Waterman and Perquin in their recent papers, in which they suggested that the Bergius process was only operative in such substances as possessed elements or groups capable of uniting with hydrogen. For example, they took paraffin wax and they could not Berginise it. If, on the other hand, a Mexican asphalt containing sulphur, or a petroleum which was known to contain oxygen, or other material containing oxygen or sulphur were used, then Berginisation proceeded. Waterman stressed the point that it was the presence of the oxygen or the sulphur or the particular group which could be attacked by hydrogen that made or did not make for the success of the operation. Dr. Thole had referred to

the experiment that had been made with silica tubes. That was the first time, he thought, they had actually seen cracking going on and the very peculiar phenomenon of the cracked spirit resting on top of the oil that was being cracked in a definitely marked layer. With regard to Dr. Perkin's criticisms, he felt sure Dr. Perkin realised that the authors had not omitted any reference to the Perkin's and Fenchell patent purposely. It was simply due to the fact that that patent was discussed in the last paper read eight years ago. Furthermore, the authors confined their present paper to processes of which they had personal knowledge. In reply to Mr. Lomax, that gentleman would see that the very appropriate word "substantial" covered the point he made in regard to liquid phase cracking. The figures Mr. Lomax quoted with regard to the coke produced in the high pressure experiment to which he alluded were very interesting. To produce a cracked residue with that small amount of coke was really an achievement. He thought Mr. Lomax would remember that in their previous paper they drew attention to the similarity of the products made from all sorts of different oils, a very striking fact. They also at that time specially pointed out that in every paper that had been published dealing with the pyrolysis of hydrocarbons within certain temperature limits naphthalene was inevitably obtained, whatever the starting out material was. With regard to Mr. Cunningham Craig's contribution to the discussion he did not think any chemist present would deny that he was other than an artist. It seemed perfectly clear to him that the exercise of chemistry was a very fine art.

The President, in proposing that a hearty vote of thanks be accorded to the authors for their excellent paper, said he thought it would be agreed that a most interesting discussion had taken place, and that the first Meeting of the Session, which had been so well attended, had been eminently successful.

The resolution of thanks was carried with acclamation and the meeting terminated.

The following written contributions to the discussion were subsequently received :—

From Mr. Arthur A. Ashworth.

The authors have pointed out that no great advance has been made in the chemistry of cracking during the past few years, but these years have been remarkable in the progress of the engineering of cracking and this progress has resulted in the installation of a large number of commercial plants.

Previously, all commercial cracking installations were on the main lines of the Burton process. Large capacity stills were used

in which the oil was distilled and cracked and from which the vapours were roughly fractionated in a dephlegmator, the heavier portions returning to the still and the lighter being condensed either under pressure or at atmospheric pressure.

Such installations are costly in capital expenditure and in operation expense, which includes fuel, material and labour. They are not very safe to operate, partly on account of the large volume of oil under high temperature and pressure and also because of the inevitable deposit of carbon on the heating surface.

As the authors have stated, attempts at vapour phase cracking have not proved successful commercially. Not only is it difficult to produce a satisfactory product from vapour phase cracking, but engineering difficulties are great. One reason for this is that the heating surface must be kept at too high a temperature for safety or long life. In liquid phase cracking, the transmission of heat from the heating surface to the liquid is rapid, so that the temperature of the wall of the still is only a few degrees above the cracking temperature of the liquid. In vapour phase cracking, the transmission of heat from the wall of the cracking chamber to the vapour is slow, so that this wall will be at a temperature roughly half way between the cracking temperature and the temperature of the furnace. This results in the steel being subjected to 800 to 900° C. and this is too high for long life of the plant. A typical example of vapour phase cracking was the Rittman process, developed during the war for the purpose of producing benzene and toluene. Commercial plants were erected and operated by the Aetna Chemical Company and by an oil company at Oil City, Pennsylvania, but I believe that one cause of the failure of these plants was the short life of the cracking tubes.

In the Ramage experimental plant described by the authors of the paper, the cracking tube was heated by electrical means, which would evidently modify this difficulty. It would be interesting to know whether the same means has been used in the commercial plant at Tulsa.

The main fact which has rendered possible the development of cracking on a commercial scale is the recognition of the effect of the time factor in cracking. Cracking is not complete as soon as an oil has been raised to the cracking temperature, but a considerable period elapses before equilibrium is reached and the full amount of inevitable carbon deposited. This enables the heating to be done in one portion of the plant and the deposition of carbon in another, so that heating surfaces are kept substantially free from deposit. This has resulted in the liquid phase cracking plants described by the authors of the paper having a strong family resemblance in that they all consist of a pipe still for the heating of the oil, a reaction chamber where the cracking is completed and

certain fractionating devices. The pressures used, however, vary greatly, from 150 lbs. per sq. in. in the Dubbs process to 600 lbs. and over in the Cross process. Chemically there is no great difference in the products. The chemical differences would seem to exist mainly in the smaller percentage of uncondensable gases formed under the higher pressure and in the character of the residue. In the Dubbs process the residue contains a considerable amount of so-called colloidal carbon, which prevents it being marketed unless it undergoes a process of settling, whereas in the Ellis and Cross processes a marketable fuel oil is produced free from suspended carbon.

The variation of pressure entails, however, considerable differences in engineering. The lower pressure used in the Dubbs process enables large capacity reaction chambers to be constructed with capacity for a considerable amount of coke. The high pressure used in the Cross process necessitates a reaction chamber of much more limited capacity. The Dubbs plant is, therefore, able to handle the residuum from a highly asphaltic oil without primary distillation, whereas in the Cross plant such oil must be first distilled to get rid of the coke-forming asphalt. This, however, is done very conveniently and cheaply in the additional pipe still, the fuel used amounting to about 2½ per cent. of the raw oil.

A great difference is also entailed in the handling of the vapours from the cracked oil, and in the fractions which are retained in the liquid phase during cracking. At a pressure of 150 lbs. per sq. in. and a temperature of 450° C., oils having a mean boiling point of 310° C. will pass into the vapour phase and so more or less escape cracking, whereas at a pressure of 600 lbs. per sq. in. and the same temperature, only oils having a mean boiling point of 200° C. will vaporize. For this reason, the Dubbs process is not adapted for the cracking of kerosene distillates, but the Cross process can crack these and obtain an excellent yield. Of course it may be urged that the usual raw material for cracking consists of gas oil, but it must be remembered that it is generally necessary to handle, not only the raw material but also the heavier fractions of the cracked distillates. The unsaturated nature of these prevents their being marketed profitably as kerosene so that they are best recycled through the plant for ultimate conversion into motor spirits.

In the Dubbs process with its smaller working pressure, a considerable range of fractions is present as vapour and this enables a rough fractionation to be effected while under pressure and some of the heavier fractions refluxed to the cracking zone. In the Cross process, as only the motor spirit fraction is in vapour form no refluxing can be performed under pressure. In this process the vapour and cracked oil escape together into an expansion chamber under reduced pressure, and the internal heat in the cracked oil is

sufficient to vaporise all but about 10 per cent. or less which is drawn from the plant and used as fuel. All the vapours from this expansion chamber pass to a very well designed tower of the Heckman type in which motor spirits of any desired end point escape to the condenser from the top of the tower and the remainder, which constitutes stock to be recycled through the plant, is drawn from the bottom. So perfect is the separation effected that the end point of the motor spirits is some 10° C. below the initial point of the recycle stock. In the Dubbs plant, the fractionation taking place under pressure, no such perfect fractionation can be effected within the plant and rerunning must be resorted to.

The advantage of producing a motor spirit of the requisite distillation range direct from the plant is, however, lost to a certain extent at present owing to the fact that no method of treatment has yet been devised which does not entail a redistillation. Silica gel was expected to accomplish this but recent reports do not indicate sufficient success for this method.

Refluxing within the plant, as effected in the Dubbs process, has some advantages and some disadvantages. One advantage is that such fractions as are refluxed and passed through the cracking zone a second or third time without passing outside the plant, have not to pay the royalty demanded on material fed into the plant. The disadvantage lies in the fact that a large amount of this refluxed material is oil having a mean boiling point above that required for motor spirits and below 310° C. so that the passage through the plant mainly consists of a series of redistillations without cracking. Such redistillations use up heat in spite of some of the heat given up in the dephlegmator being used to heat up the incoming raw material, and it is for this reason that the Dubbs process requires a larger amount of fuel when a light distillate is used as raw material, than when a heavy residue, which has few of these light fractions is run. This also accounts for the higher fuel consumption in the Dubbs process than in the Cross.

One great need in cracking is an efficient process of treatment, which will remove the gum-forming constituents of cracked motor spirits, preferably without necessitating a redistillation. In English markets, great stress is laid also upon the smell, and I have been assured that cracked spirits will never be welcomed in England unless they can be made to smell identically the same as straight run spirits. It would seem that English buyers of motor spirits require these to put on their pocket handkerchiefs rather than to burn in a motor car.

From **Professor A. W. Nash.**

With regard to the statements on vapour phase cracking, everyone now agreed, he thought, that cracking in the vapour phase

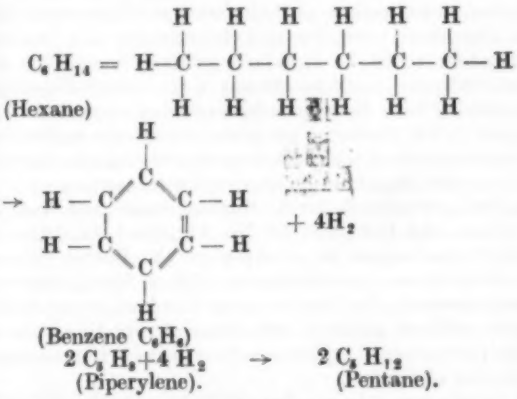
was not so attractive a commercial process as the liquid phase method.

One point should be emphasised in regard to the use of high pressures; whilst pressure is a factor of lesser importance than either temperature or time of reaction, nevertheless he thought it of considerable importance from the practical standpoint in that pressure enabled the reactions, which would otherwise require considerably more heat, to take place at lower temperatures.

A higher loss, in the shape of permanent gas and carbon deposition also obtained as a result of increased pressure, together with an increase in the yield of petrol probably due to polymerisation of the gases.

As a result of experiments carried out by him in the vapour phase it was found that increase in pressure brought about a decrease in the percentage of unsaturated hydrocarbons formed and an increase in the percentage of aromatics. It would be interesting to hear the authors' experiences in the liquid phase in this connection.

The possible reason for this, in the writer's opinion, is that the molecules of the indigenous or synthetic paraffins were probably compressed into ring compounds with the consequent liberation of hydrogen and the saturation of the olefines by these released atoms, so:—



The descriptive matter relating both to the Dubbs and Cross methods were familiar to all who kept abreast of current literature on the subject in that the manufacturers had advertised the claims of both plants extensively. When such matter was included in a scientific journal to be read by members, many of whom were abroad and out of touch with modern thought, he considered it should have been made more clear how many of the statements

represented the claims of the manufacturers and to what extent the information given was substantiated by the actual experience of the authors.

It was the opinion of the writer that no really satisfactory commercial cracking process had yet been devised in that the deposition of carbon was bound to arise in any plant designed for pyrogenic decomposition where hydrogen was not introduced.

In cracking, hydrocarbons were heated to a temperature sufficient to bring about a tendency to decompose, and although such temperature was not sufficient to split up all the compounds into their elements, nevertheless where complex molecules were converted into simpler molecules and more complex molecules, complete decomposition of some of the compounds would, of necessity, take place.

That this carbon deposition would take place not only in the chamber designed for its collection, but also throughout that portion of the plant leading to the chamber must be recognised and admitted by the manufacturers of those cracking plants described by the authors, in that the Dubbs process runs continuously for five days only and the Cross plant for from one to three weeks before stoppage for cleaning.

The whole of the coke deposition in these plants could not take place in the reaction chamber, as if this were so there would be no necessity to close down every few days for cleaning as a number of reaction chambers could be installed, whereby each one, as it became filled with coke, could be cut out of the circuit and emptied without interfering with the continuous cycle of operations.

With regard to the Carlton Ellis plant, unless the authors confirmed the statement that the gasoline produced could be treated as a straight run spirit, it should be accepted with caution.

The same claims were made for the Burton process, but Waterman and Reus (Chem. and Ind., Vol. 43, No. 11, March 14, 1924), as a result of their experiments in cracking on the Burton principle, could not substantiate this statement. They found that when working under pressure, the heavier gases dissolved in the distillate and a greater yield of gasoline was obtained, but this yield contained a high percentage of unsaturated compounds when compared with straight run distillate.

It would be of interest to members to learn whether the authors considered a yield as low as from 10 to 30 per cent. of light spirit from the Auld, Dunstan and Herring process a commercial proposition, and if so what was intended to be done with the residues.

The cost of pressure cracking, where the pressure was produced by vaporisation of some of the oil and not by the introduction of gases, was undoubtedly high, and the economy of cracking depended entirely on whether the operator was attempting to produce a

synthetic motor fuel to compete in price with ordinary straight run gasoline, or simply to blend with straight run spirit.

Whilst much had appeared in the technical press from time to time on the discoveries made by various inventors, the fundamental principles of the present-day successful cracking methods were identical with those of the Dewar and Redwood process, and it was surprising how many of the methods since invented ever got through the patent office.

The work of Waterman and Perquin on the hydrogenation of paraffin wax, referred to by the authors, tends to show that the hydrogen which is absorbed is re-evolved in the permanent gases, and hydrogenation would appear not to have taken place.

Actually it has been shown in some researches carried out by H. G. Shatwell at the University of Birmingham that the hydrogen contained in the evolved methane was greater than that which was removed from the hydrogen atmosphere. In other words, although the experiments were performed at high pressure of hydrogen, the oil had actually suffered dehydrogenation.

When, however, hydrogen was replaced by nitrogen, the quantity of methane evolved was substantially the same, although there was no free hydrogen taking part in the reaction, while the products had consistently higher iodine values.

Consequently, it follows that in the presence of hydrogen, hydrogenation and dehydrogenation proceed simultaneously, whereas with nitrogen, dehydrogenation only occurs. Further, the products resulting from hydrogenation, though not differing markedly from those obtained in absence of hydrogen, are the more stable, keep better in storage, and have not a pronounced cracked odour.

If the object of hydrogenation is to break down long-chain hydrocarbons and obtain smaller molecules of the same series, then it is doubtful if success will result. There is strong evidence, however, to support the hypothesis that considerable proportions of aromatic hydrocarbons are produced, and although these contain a low percentage of hydrogen, they are saturated to iodine and are admirably adapted for use in light internal-combustion engines. These points will be dealt with in more detail in a paper to be published shortly.

From Mr. R. G. Neilson.

The authors are to be congratulated on their paper, which, if one may be permitted to be alliterative, is a clear, concise, and yet comprehensive survey of recent developments in "cracking," and indicates that this hitherto purely empirical process is gradually moving from the realm of an art to that of an exact science.

Our knowledge of the conditions governing the economical cracking of petroleum is appreciably contributed to by the authors,

particularly as a result of the careful observations recorded during development of the A.D.H. experimental plant from its initial stage, when Drs. Dunstan and Thole were primarily concerned in destroying the gelling properties of heavy residue by heat treatment with production of cracked products as a secondary consideration only.

A works unit based on the latest development of the small scale plant is now under construction, and it is confidently anticipated that operating results will parallel those of the latter, and be equal to, if not better than, results of any moderate pressure process in use.

In regard to vapour phase cracking, the authors rightly state that it compares unfavourably with liquid phase in regard to carbon formation, losses, and quality of products. The claims, in the cases of the Ramage or Noad processes, for the action of the so-called "catalysts," such as ferric oxide and metallic iron packings, are based on mythical assumptions. The packing in these steam and oil vapour processes does not act as a catalyst, but becomes permanently coated with the stable black oxide of iron. Some years ago, in the course of some experiments, I found this to be the case as expected, and further that a packing of any refractory material in the cracking tube would yield, under equivalent temperature and water or steam and oil feed conditions, almost identical percentage and quality of cracked products.

The phenomenon in these cases is evidently one of molecular disruption of the oil caused by heat, the packing in the tubes assisting in the operation by providing a certain resistance to the free passage of the oil vapours and increasing the heated surface area to which they are exposed. A certain amount of hydrogenation no doubt also takes place as a result of ordinary dissociation of steam.

A point of importance in the successful evolution and further development of moderate pressure liquid phase processes of the nature of the Carleton-Ellis, Cross and A.D.H., using pressures from about 400 to 700 lbs. per sq. in. in the reactor vessels, is the effect of continued heating and cooling on the molecular structure of the steel of these vessels, any change in which might give rise to risks of explosion, and this applies to a much greater degree in high pressure processes.

We have no definite information on the point, which is one that would repay experimental investigation, as on the large scale it may be necessary to have some knowledge of the safe life of a reactor vessel.

STUDENTS' SECTION PRIZE PAPER, 1923-24.

The Rumanian Oilfields.

By Lieut. J. H. Blakiston, R.N.R.
(Student Member).

Petroleum has been known to exist in Rumania since remote times from the existence of numerous hand-dug wells in the Prahova and Bacau districts, and also by the use of the Wallachian word "pacura" (meaning petroleum) in the naming of towns—*e.g.*, Parcureti.

In the year 1750 a traveller named Raicevich reported that "liquid bitumen" was found in Rumania and used for such purposes as medicinally treating cattle, lighting, axle grease, etc.

The most prolific spring at this time appears to have been near Parcureti, in the Prahova district, which, together with neighbouring sources, gave an annual production of 20 tons.

As far back as 45 years ago there were refineries, more or less satisfactorily conducted, in the larger towns where oil was collected and treated by merchants; while still larger quantities passed over the frontier to be dealt with by more elaborate plant—*e.g.*, Kronstadt (now in Greater Rumania) and Galicia.

The oil business may be said to have started in a systematic manner from 1866, the year in which the Government redistribution of land took place.

Comparing Rumania with Galicia, we find that in the former country the entire production was from hand-dug wells long after borings by steam power had been made in the latter; it is, indeed, only within the last 33 years that drilling has superseded digging in Rumania. In 1890 many properties had changed hands, numbers of small interests had amalgamated and the business generally had been put on a firm footing. About this time the first large oil company of Rumania was formed. It secured the control of the greater part of the country's production, which was at that time obtained from Glodeni (Dambovitza), Campina (Prahova), Sarata (Buzeu), and Solontz (Bacau), the total output being about 60,000 tons a year. This company refined the oil at Bucharest, Monteoru, Campina, and Moinesti, and possessed pipelines for the transportation of the oil from Glodeni to Doicesci and from Bustenari to Doftana.

In 1895 the business just described was acquired by the Steaua Romana; other companies were now formed and the production rapidly increased. In 1896 the Steaua Romana erected tank storage at Giurgiu and Ratisbon, between which places oil was

transported in tank barges with a view to supplying Germany and Switzerland. Storage was also provided at Constanza so that oil could be shipped to Mediterranean ports.

Home consumption grew rapidly and liquid fuel came into use. In 1908 the Rumanian railways used 180,000 tons, it being utilised as locomotive fuel in conjunction with lignite.

In 1910, 600 locomotives were using this fuel, and it was also in use to a large extent as a fuel for brewers, engineering works, electric generating stations, etc., etc.

The estimated production from 1895–1900 will give an idea of the development of the industry:—

1895	.. ..	76,000 tons
1896	.. ..	80,000 ,,
1897	.. ..	110,000 ,,
1898	.. ..	180,000 ,,
1899	.. ..	250,000 ,,
1900	.. ..	250,000 ,,

This lack of increase in production was due to industrial depression and other causes, but matters improved in 1901, and subsequently there was a steady growth in the output.

In 1908 the production had risen to 1,147,727 tons and increased to 1,352,289 tons in 1910. 1913 showed a production of 1,818,177 tons in spite of the fact that from June to August in that year the army was mobilised, causing shortage of labour and many other difficulties.

The Great War caused a slight fall in the years 1914 and 1915—*viz.*, 1,781,078 tons and 1,562,803 tons respectively, and this shows up the remarkable organisation of the Rumanian oil industry and its ability to quickly adapt itself to changing circumstances. Enormous difficulties were met with during these two years, including scarcity of labour, shortage of supplies, partial cessation of exports and the resulting accumulation of stocks.

Rumania entered the Great War in September of 1916 and serious injury to the industry was caused, as at the end of this year the stocks of oil were destroyed and wells were plugged to hinder Germany from obtaining supplies during her occupation.

This damage was largely repaired under German control, and the production was raised from 373,000 tons in 1917 to 950,000 tons in 1918.

Since the war every effort has been made to repair the damage done, and the production for 1921 was 1,149,636 tons.

Bustenari was the first field to attract serious attention and it was this field which first established the reputation of Rumania as an oil-bearing country. This oil was of asphaltic base, contained a high percentage of illuminants (a very important product of oil at that time). The next field to receive attention was Campina

which lies on the same anticline, four miles to the west from Bustenari.

Moreni was the next important field to be opened up, and hand-dug wells had long been worked on this field.

Wells up to 2000 feet in depth gave a good production, and Beeby Thompson states that in 1912–14 one well yielded 400,000 tons. Moreni Bana was a field which presented many peculiar features; it was a shallow field of limited proportions, producing an oil exceptionally rich in benzine (40 per cent.).

In 1914 a lower horizon was struck and several large flowing wells were brought in. This field has now been exhausted.

Several other fields were located to the east of Moreni and on the same anticline, the most important being Filipeshti and Baicoi, being respectively 5 and 10 miles distant.

There are many other small fields, such as Solontz, Zamesti, etc., etc., together with 35,000 acres of known oil land not yet developed and about 300,000 acres of probable oil lands to be prospected.

About 85 per cent. of the production of Rumania comes from the Prahova district—*i.e.*, Moreni, Bustenari, Campina, etc.

The town of Plocesti (50,000 inhab.) may be said to be the centre of the industry, and here the majority of the refineries are situated.

Plocesti is connected with the important fields by a series of pipe-lines, and a trunk pipe-line connects this town with Constanza, a distance of about 150 miles.

The oil is dark brown in colour, and has a specific gravity of from 0·824–0·840, though oils of 0·780 and 0·890 are obtained in some fields.

About half the output is available for export and, in pre-war times, the United Kingdom, France, Germany and Egypt were the best customers. In 1920 the refineries treated 947,289 tons.

Benzine	208,821
Kerosene (115,934 tons of these used as fuel)	193,757
Sundry oils	79,990
Residual oils	465,721
Total	947,289

Geology.

Rumania is divided into three physiographical zones (see Fig. 1): The Carpathians, the Foothills and the Plains.

The Carpathians may be subdivided into two groups—(*a*) an inner one composed of Mesozoic, metamorphic and igneous rocks, (*b*) an outer zone composed of the earlier Tertiaries and known as the Flysch. Flysch is a term given by German and Austrian

geologists to a certain formation found in the geology of Switzerland. It is a general term embracing a formation composed of sandstones, shales and conglomerates which have been mainly derived from the Alps.

This formation forms mountains of 6000 feet in some cases. Fossil evidence shows the Flysch to be of Oligocene Age.

Subdivision (*b*) of the Carpathians resembles this Swiss formation, and is known, therefore, as the Flysch.

The oilfields are usually in the Flysch and Foothill areas. It should be noted that the oilfields lie to the north (Galicia), east (Bacau district), and south (Prahova district) of the Carpathians, all being on the eastern side of this mountain range.

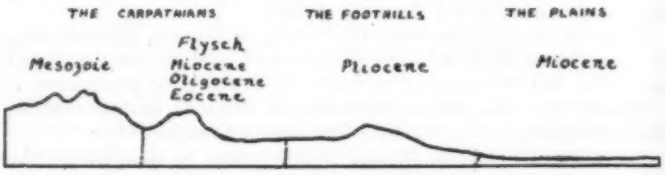


FIG. 1.

THE PHYSIOGRAPHICAL ZONES.

The formations we are concerned with are as follows:—

LEVANTINE DASIC PONTIC MÆOTIC	PLIOCENE.
NEUTRAL ZONE.	
SARMATIC SALIFERE	MIOCENE.
OLIGOCENE.	
EOCENE.	

As I do not intend to deal wifh the Pliocene to any extent, I will go on to the Miocene, Oligocene and Eocene and describe the beds found in these formations.

The upper Sarmatic does not exist. The middle is rare and is of fresh water origin.

The lower is a grey, yellowy sandy formation intercalated with bands of marl; near its base bands of Andesitic tuff are found. Foraminifera are found throughout the series.

Neutral Zone.—This is due to the fact that the demarcation between the Sarmatic and Mæotic is very poor. (This may account for the fact that geologists appear to be undecided as to whether the Mæotic is Lower Pliocene or Upper Miocene.)

The Sarmatic is as often as not absent when the Mæotic runs straight on to the Salifere—*e.g.*, Campina, Baicoi and Moreni.

The Salifere can be divided thus :—

1. Grey argillaceous sands, sandstones, andesitic tufts and andesitic sills.
2. Marls with gypsum.
3. Red horizon with traces of oil, containing globegerinai.
4. Conglomerate with Eocene fragments, Carals, Pecten, Cerithuim marganataceum (probably from Oligocene).
5. Cornu formation. Lowest horizon contains gypsum, pure salt and a certain amount of oil generally. Also a conglomerate of which 1 sq. cm. pebbles of limestone are characteristic.

   (A well-known Rumanian geologist refers to Cornu as "The Mother of Petroleum.")

The upper argillaceous beds of the Salifere very closely resemble the clever sandstone of the Oligocene, but the former can always be recognised by the fact that they contain Hornblende grains.

One peculiar feature of the Salifere is that it frequently intrudes, like an igneous dyke, into the overlying beds.

It is possible that the fossils found in the Salifere are derived from the Oligocene.

The Oligocene may be divided into three zones :—

1. Clever sandstone, possibly of terrestrial origin. A sharp compact sandstone very light in colour and never calcareous, it contains little mica.
   These points are most important as the Eocene sandstone is almost identical with it, the only differences being that it contains much muscovite and is calcareous.
2. *Tchepota.*—Menilite shales, dark in colour, calcareous, fossiliferous, characterised by bands of Hornstone (siliceous sinter).
3. Sipot Limestone, blue to dark browny blue, together with a highly siliceous sandstone. Mudstones slightly calcareous and fairly thinly laminated.
   The Eocene consists of the Jargu Ocna schists. They are usually red and green in colour and contain lenticles of the Moinesti sandstone and thin bands of limestone.
   Below the beds we find a series of coloured marls which usually contain lenticles of a green conglomerate at their base. This conglomerate is glauconitic in character and is most probably derived from the underlying Cretaceous beds.

The Moinesti sandstone is light in colour, calcareous, contains much muscovite, also nodular concretions and nummulites are frequently found in it.

The Lower Eocene is never represented.

Fucoids are very common in the Eocene ; indeed, it was usually very easy to find the junctions between the Eocene and the Oligocene by observing the following points :—

1. Soil hard and green in colour.
2. Marshy vegetation, due to the marls.
3. Calcareous sandstone with abundance of muscovite.
4. Presence of fucoids in dried marls.

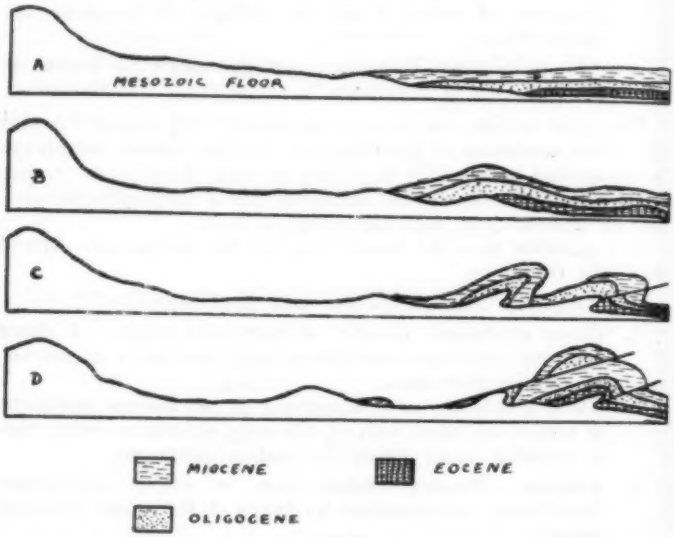


FIG. 2.

THE FORMATION OF NAPPES.

The Bacau District.

The author spent a month in mapping the areas surrounding Zamesti, a small village in the Trotus valley and some 10 km. to the north of Moinesti. This area consists of Eocene, Oligocene and Miocene strata complexly folded in a series of Nappes.

English literature on this theory is limited, but much has been written in German. Fig. 2 shows how the Nappes were most probably formed.

The oil is generally found to exist in the beds of the Nappe where they rest on the Salifere.

Oil is nowhere found in commercial quantities in the Salifere, yet everywhere it contains traces of oil, and wherever suitable beds recline or overlie it they are found to contain oil. Such beds may, of course, be of pre- or post-Miocene age.

The daily routine of the party consisted of combined mapping, surveying and fairly energetic mountaineering, from 7 a.m. to sometimes as late as 8 or 9 p.m. Maps of the area, contoured every 100 metres, were provided, but proved to be far from

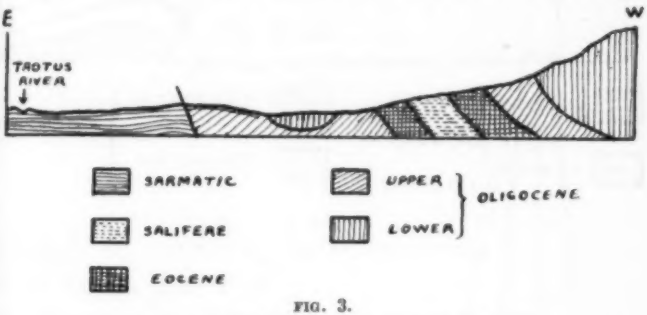


FIG. 3.

DIAGRAMMATIC SECTION OF THE TROTUS VALLEY.

accurate, and as few of the buildings in the surrounding villages were permanent enough to be marked on the maps it was necessary to fix landmarks, by means of cross bearings, which would be suitable for taking a departure bearing before striking off into the woods. The hills were in some cases nearly 3000 feet high and thickly wooded, so that very careful compass traverses were necessary for accurate mapping. The instruments issued were: A compass, aneroid barometer, and clinameter. The aneroid barometers were surprisingly accurate and extremely useful when the map happened to be correct and the observer had remembered to set it in the valley before starting out for the day.

There were many magnificent exposures, in the numerous small gulleys, showing the complex nature of folding, and one point which was most noticeable was the effect of soft strata when folded between comparatively hard beds. In cases where the hard bands were gently folded the sandwiched soft strata was considerably distorted, thus offering a warning to those who are tempted to take the dip of soft strata which have been so placed.

Fig. 3 is a typical section of the Trotus Valley.

The oil of the Campina field is contained in the Pliocene beds which both recline on and overlie the Miocene as shown in Fig. 4. The oil is said to be derived from the Salifere and the Sarmatic.

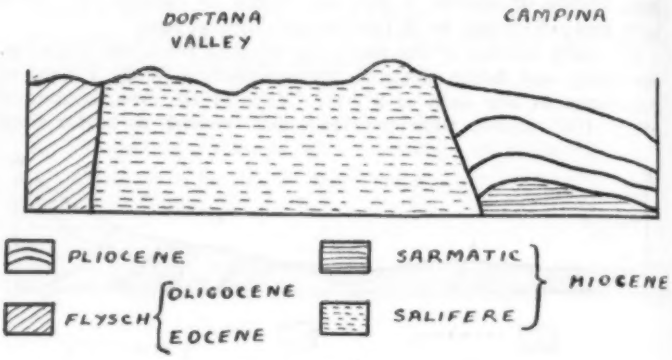


FIG. 4.

DIAGRAMMATIC SECTION OF CAMPINA.

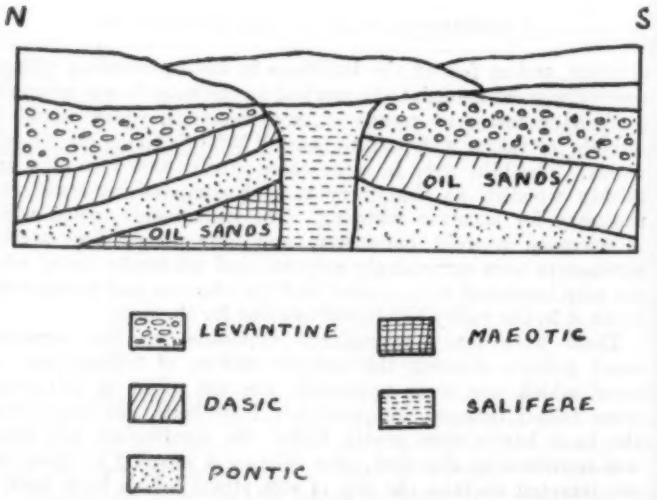


FIG. 5.

DIAGRAMMATIC SECTION OF MORENI.

Fig. 5 shows the structure of the Moreni field. According to one theory this structure is a denuded anticline, and the cone-shaped cave of Salifere worked its way up through the softer Pliocene beds much in the same way as a thorn will work its way out of the hand.

It will be seen that the producing beds of the north side are in the Mæotic and those of the south in the Dasic.

On the northern side the oil is contained in the Mæotic and to the south in the Dasic. The popular theory is that on the north side upward migration was arrested by the Pontic clays,

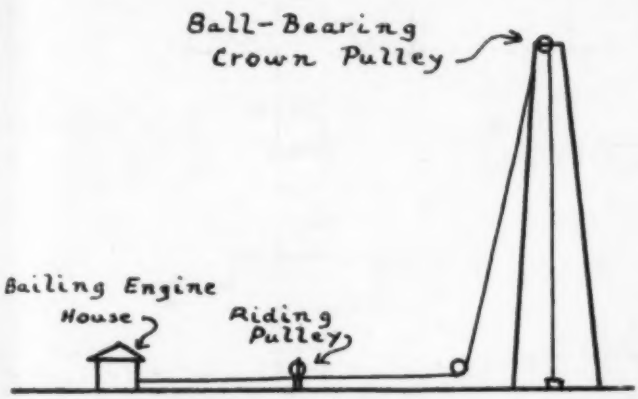


FIG. 6.

LEAD USED FOR BAILING.

but on the south side it is supposed to have migrated through fissures in this same formation. There is little oil in the upper Dasic beds, and, therefore, it had no temptation to move into the overlying Levantine gravels.

The oil of this field in all probability originated in the Salifere, One theory accounts for the formation of oil in the Salifere by stating that the animal and vegetable constituents of the oil were preserved from oxidation by the salt contained in these beds.

Field Engineering Notes on Moreni.

Moreni is the most important field of Rumania, and here the most up-to-date drilling plant in the country is to be found.

Production is commonly carried out by bailing, owing to sand difficulties, though swabbing and pumping is used in isolated

cases. (Experiments have also been carried out with the air lift, but without success.)

Many ingenious devices are used on this field. For instance, diagram (6) shows a lead which is sometimes used when bailing a gassy well so that a ball-bearing crown block may be used. The whip, due to the baling line unreeling from the drum, is taken up by a riding pulley.

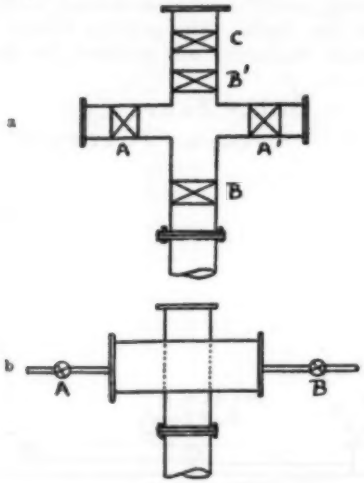


FIG. 7.

TYPES OF BLOW-OUT PREVENTERS.

Another experiment of interest was noticed. When the oil level of a very gassy well was required to be known, the bailer was lowered slowly into the well and the gas rising from the casing head watched. When this gas momentarily ceased to rise, the bailing line was marked and that level taken to be the oil level. (This phenomenon has a very simple physical explanation.)

The wells brought it on this field have a tendency to flow, therefore a casing head valve as shown in Fig. 7 (*a*) is set before the producing bed is reached. After oil has been struck the column of water in the well is bailed until such time as the pressure below overcomes it. At this point the bailer is rapidly withdrawn.

The well is closed down and valves B, A and A^1 are then opened and the well brought in. These valves are controlled from a hut about 30 feet distant from the well, and a pressure gauge is fitted here so that "closed down pressure" may be observed.

A hydraulic casing head valve is favoured by one company. It consists of a barrel as shown in the diagram, in which a piston works which may be moved across the casing head so closing in the well. It is actuated by admitting water under 2 or 3 atmospheres of pressure, the valves A and B alternatively becoming inlet and exhaust (see Fig. 7 (*b*)).

Drilling.—This formation is favourable to rotary drilling, and this system is gradually superseding the older plant.

The well is drilled by the rotary within 30 or 40 meters of the producing bed, when the rotary plant is removed to a new well site and the Canadian cable plant takes its place.

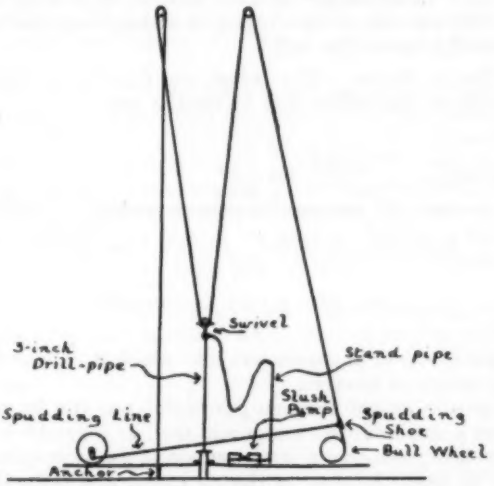


FIG. 8.

THE INDIAN SYSTEM.

The well is then drilled in by this latter system thus enabling the operator to observe the exact depth at which the producing bed is struck and more accurate geological data to be obtained.

The danger of mudding up the oil sand is also obviated.

Many other systems, however, are in use on this field including the Canadian pole, Pennsylvanian and several percussive mud-flush systems such as the Fauck, Rapid Alianta and the Indian.

The majority of these systems is, of course, well known to all those connected with the industry, but one of more local application is the Indian system, and a short description may be of interest.

The Indian System.—The bit is lowered on a 3-inch drill-pipe, the joints of which are carefully made. A swivel is connected to the top joint and a flexible hose connects it to the stand pipe as in the Rotary system. The mud circulates down the drill-pipes, out through a hole in the bit and returns up the casing. The string of tools is suspended in the hole by means of a single sheave moving block, through which the drilling-line is rove, the standing part of which is made fast to a suitable anchor in the foundations of the rig.

Movement is imparted to the tools by means of a spudding-line and shoe as shown (see Fig. 8).

The chief disadvantage of this method of drilling is that a considerable amount of time is lost in withdrawing the tools when it is desired to clean the well.

Fuel for the Boilers.—The boilers are fitted with both oil and gas burners so that either may be used at will.

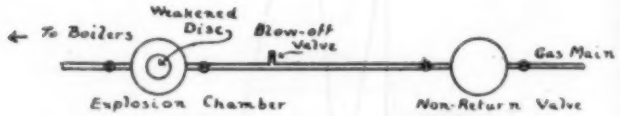


FIG. 9.

GAS MAIN SAFETY ARRANGEMENT.

The gas is stored in gasometers into which it is passed from the wells by means of blowers.

(In one case an old Paxman gas engine was run by means of a belt from a small electric motor and used as a gas blower.)

If a well is producing a large volume of gas it is quite common practice to keep the door of the rig closed and open the suction valve of the blower to the atmosphere of the closed rig. It will be seen that from this practice there is a risk of getting an explosive mixture in the gas mains and this is provided for by a safety arrangement as shown in Fig. 9.

On an explosive mixture reaching the burners it flashes back to the explosion chamber and an explosion takes place here, blowing off the weakened disc, the resulting flame being unable to reach the mains on account of the non-return valve.

When an explosion takes place the gas burners are shut off and the oil burners put into action; the gas main is opened up to the atmosphere for about five or six minutes and gas is then passed to the boilers through another explosion chamber while the one last used is under repair. These explosion chambers are used in batteries of four or five.

The Vapour Tensions of the Normal Paraffins.

By A. A. Ashworth, M.A., A.M.Inst.C.E.

The variation of the vapour tension of the normal paraffins has been investigated by Young for the series up to Octane and for the higher members by Krafft, and the results of their work has been summarised in a table given in "The Elements of Fractional Distillation," by Clark Robinson. In this table the boiling points of the nearly complete series are given at pressures of 760 mm., 100 mm., 50 mm., 30 mm., 20 mm., 10 mm., and in some cases at 5 mm., together with those of a large number of other organic substances.

The completeness of the experimental work in the case of the normal paraffins indicated that this series would be a useful one to study in the effort to evolve a law governing the variation of the vapour tension with temperature. If such a law could be found, it would have an important bearing on our knowledge of the latent heats of vaporisation of oils. Such knowledge is vitally important in refinery work, but at present we have to rely on a few scanty experimental observations and formulæ which are empirical and, it is to be feared, inexact.

The experimental observations were first compared with the approximate Clapeyron equation which may be written as follows:

$$\log_e P_2 - \log_e P_1 = \frac{L}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

where R = the Gas Constant = 1·9855.
P_1 and P_2 are absolute pressures.
L = Latent Heat × Molecular Weight.
T_1 and T_2 are absolute temperatures in degrees Centigrade.

If the pressures be measured in atmospheres and P_1 be put equal to 1 atmosphere and T_1 be the boiling point of the liquid at atmospheric pressure, = Ta, we get

$$\log_e P_2 = \frac{L}{1{\cdot}9855}\left\{\frac{1}{Ta} - \frac{1}{T_2}\right\}$$

But von Trouton's formula for the latent heat of petroleums gives L/Ta = Constant = 20·7 whence we get

$$\log_{10} P_2 = \frac{20{\cdot}7\ Ta}{1{\cdot}9855 \times 2{\cdot}3026}\left\{\frac{1}{Ta} - \frac{1}{T_2}\right\}$$

$$= 4{\cdot}528 - \frac{4{\cdot}528\ Ta}{T_2}$$

This is a straight line equation between $\log_{10}P$ and $1/T$ and indicates that, if a diagram be drawn with ordinates $= \log_{10}P$ and

abscissæ $=1/T$, the relation between the vapour tension and pressure of any oil will be a straight line drawn through a point on the vertical axis 4·528 above the origin and passing through the point on the horizontal axis representing $1/Ta$, for, if T be put equal to infinity, $\log_{10}P=4·528$ and if P be put $=1$, $1/T=1/Ta$.

Unfortunately, this approximate equation proves on trial to be hardly within the limits of approximation. The following table gives the observed and calculated boiling points and the differences.

Substance.		B.P. at 760 mm.	B.P. at 100 mm.	B.P. at 50 mm.	B.P. at 30 mm.	B.P. at 20 mm.	B.P. at 10 mm.
n-Hexane ..	Obs.	69·0	15·6	1·5	— 7·9	—15·0	—25·7
	Cal.		13·3	— 1·8	—12·0	—19·5	—31·3
	Dif.		— 2·3	— 3·3	— 4·1	— 4·5	— 5·6
n-Octane.. ..	Obs.	125·8	65·6	50·2	39·3	31·3	19·1
	Cal.		60·8	43·2	31·4	22·6	8·8
	Dif.		— 4·8	— 7·0	— 7·9	— 8·7	—10·3
n-Decane ..	Obs.	173·0	107·0	90·0	78·0	68·0	55·0
	Cal.		100·4	80·7	67·4	57·6	42·2
	Dif.		— 6·6	— 9·3	—10·6	—10·4	—12·8
n-Pentadecane ..	Obs.	270·5	194·0	173·0	160·0	150·0	135·0
	Cal.		182·0	158·0	141·9	129·9	111·1
	Dif.		—12·0	—15·0	—18·1	—20·1	—23·9
n-Nonadecane ..	Obs.	330·0	248·0	226·5	212·0	200·0	183·0
	Cal.		231·8	205·2	187·3	174·0	153·2
	Dif.		—16·2	—21·3	—24·7	—26·0	—29·8

For diagram illustrating these results see opposite page.

Examination of this diagram shows that the observed vapour tensions, instead of forming straight lines, form curves, and that the tangent to these curves even at atmospheric pressure is not the straight line given by the formula, thus indicating that the formula will not give the correct dP/dT at atmospheric pressure, and thus is useless for calculating the latent heat. Further, the tangents to the actual curves at atmospheric pressure do not meet at any one point in the vertical axis, showing that the rule of Ramsay and Young is inaccurate, for this rule states that dP/dT is inversely proportional to T.

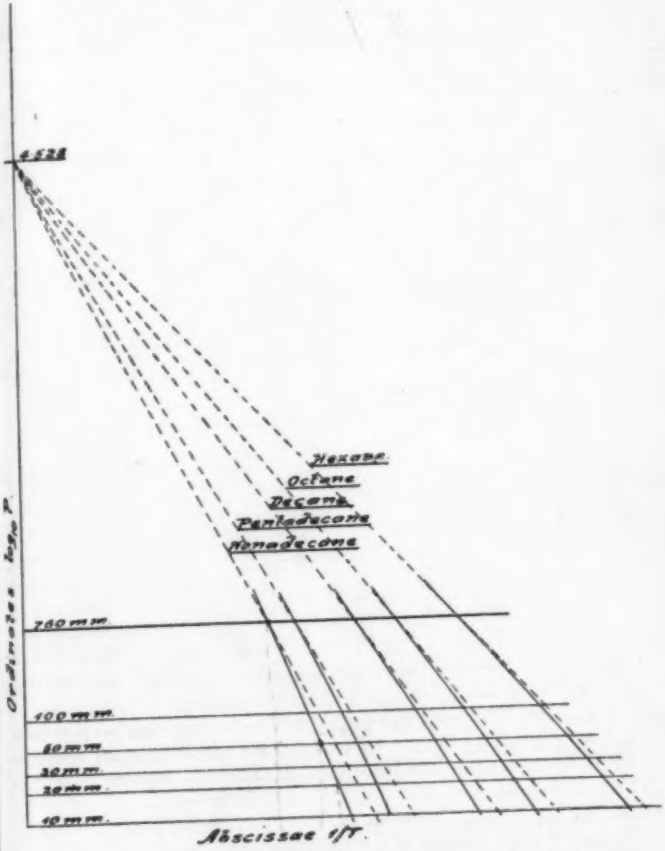
Further examination of the curves on the diagram shows that the curvature is all in one direction, and indicates that, in order to obtain a straight line diagram, we shall have to replace T in the formula

$$\log_{10}P=4·528-\frac{4.528\ Ta}{T}$$

by some function, F(T) of T which is less than T. The initial problem was, then, to find some relation between F(T) and T which would straighten the curves of all the normal paraffins.

The condition which F(T) must satisfy in order to straighten any one of the curves on the diagram is that

$$\frac{\frac{1}{F(T_1)} - \frac{1}{F(Ta)}}{\frac{1}{F(T_2)} - \frac{1}{F(Ta)}} = \frac{\log P_1}{\log P_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

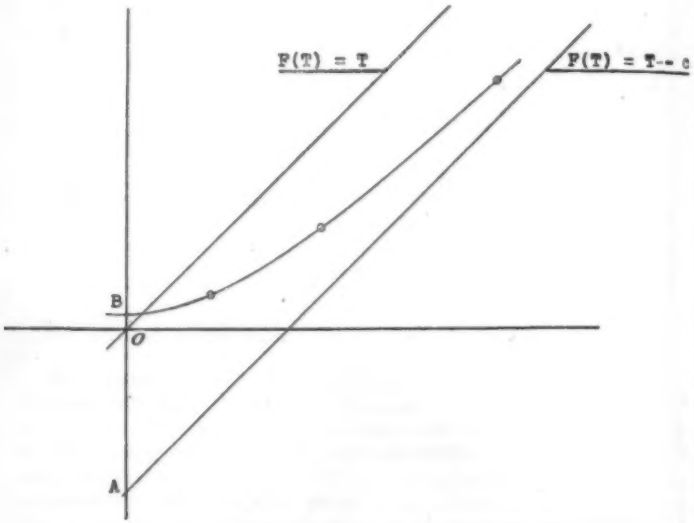


It has been shown above that F(T)=T does not satisfy the condition for any one of the normal paraffins, but that the curvature shows that F(T) must be less than T.

The next attempt to find the relation between F(T) and T was to put F(T)=T—const.

This attempt failed as, by finding the value of c which would satisfy the condition for one of the higher boiling paraffins and then doing the same for one of the lower boiling paraffins, these values were found to be different, the higher member of the series requiring a larger value for c than the lower.

It will be as well to illustrate these successive steps by drawing a diagram in which the ordinates represent F(T) and the abscissæ T.



A line at 45° through the origin will represent F(T)=T.

A second line parallel to the first and intersecting the horizontal axis at a distance c from the origin will represent F(T)=T—c.

Finding the value of c for three separate paraffins, gave roughly the three positions marked by small circles.

This showed that a rectangular hyperbola could probably be drawn to represent the relation between F(T) and T. The equation of such a rectangular hyperbola would be

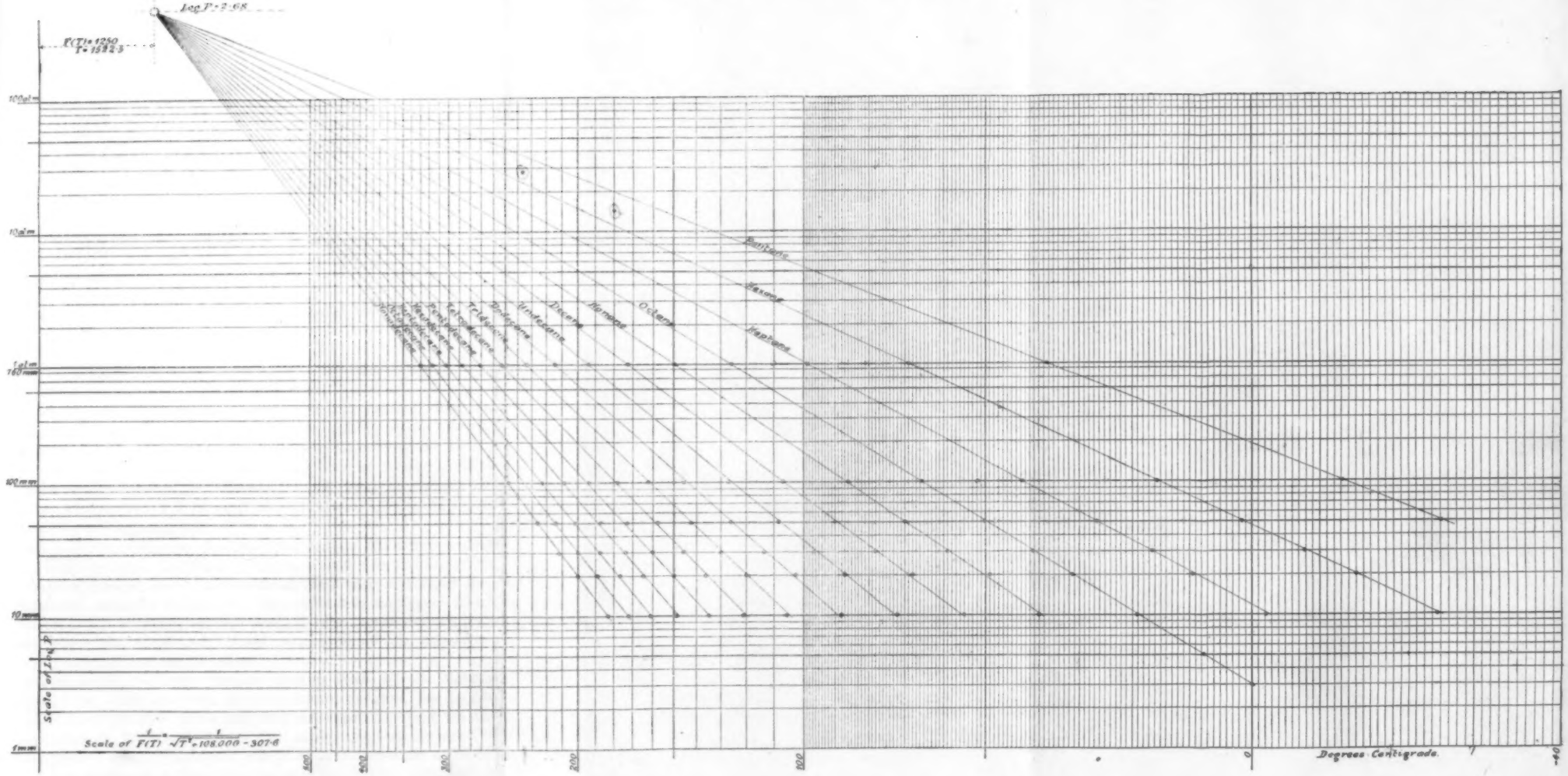
$$\frac{(F(T)+C)^2}{D^2}-\frac{T^2}{D^2}=1$$

where D=AB on the diagram and C=AO on the diagram.

This gives $F(T)=\sqrt{T^2+D^2}-C$.

VAPOUR TENSIONS OF NORMAL PARAFFINS.

Vertical Scale Log 10 = 80 mm. Horizontal Scale 88,000 ÷ F(T) = X mm.



The above expression for F(T) involves two constants, C and D. The value of these constants for two of the paraffins can be obtained by consideration of their boiling points at three different pressures say, at 760 mm., 100 mm., and 10 mm. For instance, taking Hexane and Nonadecane we get the following equations from equation (1) on p. 787.

Hexane. $T_a = 273 + 69{\cdot}0 = 342{\cdot}0$ $T_{100} = 273 + 15{\cdot}6 = 288{\cdot}6$
$T_{10} = 273 - 25{\cdot}7 = 247{\cdot}3.$

$$\frac{\frac{1}{\sqrt{288{\cdot}6^2 + D^2} - C} - \frac{1}{\sqrt{342{\cdot}0^2 + D^2} - C}}{\frac{1}{\sqrt{247{\cdot}3^2 + D^2}} - \frac{1}{\sqrt{243{\cdot}0^2 + D^2} - C}} = \frac{0{\cdot}8808}{1{\cdot}8808}$$

Nonadecane. $T_a = 273 + 330{\cdot}0 = 603{\cdot}0$ $T_{100} = 273 + 248{\cdot}0 = 521{\cdot}0$
$T_{10} = 273 + 183{\cdot}0 = 456{\cdot}0.$

$$\frac{\frac{1}{\sqrt{521{\cdot}0^2 + D^2} - C} - \frac{1}{\sqrt{603{\cdot}0^2 + D^2} - C}}{\frac{1}{\sqrt{456{\cdot}0^2 + D^2} - C} - \frac{1}{\sqrt{603{\cdot}0^2 + D^2} - C}} = \frac{0{\cdot}8808}{1{\cdot}8808}$$

We have here two simultaneous equations in D^2 and C and solving these we get

$$D^2 = 108{,}000$$
$$C = 307{\cdot}6$$

Applying these values to the observed results we find that, not only are the 760 mm., 100 mm., and 10 mm. boiling points brought into one straight line, but that the vapour pressure curves for the other intermediate members of the series become straight. This was most easily proved by drawing a diagram in which the ordinates represented $\log_{10}P$ and the abscissæ $1/F(T)$ in which $F(T) = \sqrt{T^2 + 108{,}000} - 307{\cdot}6$.

Plotting on this diagram the observed results for every normal paraffin from Pentane to Nonadecane, not only was it found that every vapour tension curve had resolved itself into a straight line, but that these straight lines all sensibly passed through one point. This point is not situated on the vertical axis but corresponds to a point where $T = 1{,}592$ and $P = 480$ atmospheres, or, otherwise, where $F(T) = 1250$ and $\log_{10}P = 2{\cdot}68$.

This convergence of the vapour tension lines of the normal paraffins to one definite point is not a mere accident due to the particular form of the curve adopted as approximating to the relation between F(T) and T, for the same result is attained if another form of curve is adopted which attains the same approximation, but indicates a definite law governing the variation of vapour tension with temperature in the case of the normal paraffins.

The mathematical expression for this law may be obtained from the above facts as follows:—

The above facts, put into words, may be stated "If a diagram be drawn on which the ordinates are the logarithms to the base 10 of the pressure expressed in atmospheres and the abscissæ are $1/F(T)$ where $F(T)=\sqrt{T^2+108{,}000}-307{\cdot}6$, then the vapour tension of any normal paraffin will be expressed by a straight line drawn through two points, one of which is that represented by $F(T)=1250$ and $\log_{10}P=2{\cdot}68$ and the other that represented by the observed boiling point of the paraffin at atmospheric pressure or where $F(T)=F(T_a)$ and $\log_{10}P=0$.

The mathematical expression for this is

$$\frac{\frac{1}{F(T_a)}-\frac{1}{1{,}250}}{\frac{1}{F(T)}-\frac{1}{1{,}250}}=\frac{2{\cdot}68}{2{\cdot}68-\log_{10}P}$$

or

$$\frac{\frac{1{,}250}{F(T_a)}-1}{\frac{1{,}250}{F(T)}-1}=\frac{2{\cdot}68}{2{\cdot}68-\log_{10}P}$$

The easiest way to apply this formula is by means of the diagram but, unless the diagram is of an unwieldly size, the readings at the higher temperatures are not sufficiently open for critical reading. For critical work a table is appended to this paper giving the temperature in degrees Centigrade, the corresponding absolute temperature, the value of F(T) and the value of the expression

$$\frac{1{,}250}{F(T)}-1 \text{ for each degree from } -40^\circ \text{ C. to } 500^\circ \text{ C.}$$

The use of this table is best illustrated by an example. Octane at atmospheric pressure boils at 125·8° C. What is its boiling point at 10 mm. pressure.

Here $\frac{1{,}250}{F(T_a)}-1=4{\cdot}976$ (from the Table)

$$\log_{10}P=-\log_{10}76=-1{\cdot}8808$$

$$\frac{2{\cdot}68}{2{\cdot}68+1{\cdot}8808}=\frac{1}{1{\cdot}702}$$

$$\frac{1{,}250}{F(T)}-1=4{\cdot}976\times1{\cdot}702=8{\cdot}469$$

and the Table gives the value of T to be 292 and thus the boiling point of Octane at 10 mm. to be 19·0° C. The observed boiling point is 19·1° C.

In a second appendix to this paper is given a list of the observed and calculated boiling points not only for the normal paraffins, but for most of the hydrocarbons for which observed results are obtainable. In the case of the normal paraffins the agreement is

very close, in fact it is possible to detect by means of the formula certain obvious errors of observation in the observed results. In the case of the other hydrocarbon series, the agreement is not so close, but is yet better than that which can be obtained by any other formula published up to the present. A close agreement for all the hydrocarbon series was not to be expected as it would entail a universal law for the variation of the latent heat with the temperature and also that the departure from the perfect gas law, $PV=RT$ should be the same for all hydrocarbons.

The law deduced above for the variation of vapour tension with the pressure is

$$\frac{\frac{1}{F(T_a)}-\frac{1}{1,250}}{\frac{1}{F(T)}-\frac{1}{1,250}}=\frac{2\cdot68}{2\cdot68-\log_{10}P}$$

This may be written

$$\frac{2\cdot68-\log_{10}P}{2\cdot68}=\frac{\frac{1}{F(T)}-\frac{1}{1,250}}{\frac{1}{F(T_a)}-\frac{1}{1,250}}$$

Or

$$\frac{\log_e P}{2\cdot68\times2\cdot3026}=\frac{\frac{1}{F(T_a)}-\frac{1}{F(T)}}{\frac{1}{F(T_a)}-\frac{1}{1,250}}$$

Differentiating we have

$$\frac{1}{6\cdot171}\frac{dP}{P\,dT}=\frac{1}{\frac{1}{F(T_a)}-\frac{1}{1,250}}\left\{\frac{1}{F(T)^2}\frac{dF(T)}{dT}\right\}$$

But $(F(T)+307\cdot6)^2-T^2=108,000$
and differentiating

$$2(F(T)+307\cdot6)\frac{dF(T)}{dT}=2T$$

or $$\frac{dF(T)}{dT}=\frac{T}{F(T)+307\cdot6}$$

whence

$$\frac{1}{P}\frac{dP}{dT}=\frac{1,250\times6\cdot171}{\frac{1,250}{F(T_a)}-1}\times\frac{1}{F(T)^2}\times\frac{T}{F(T)+307\cdot6}$$

The values of $\frac{1,250}{F(T)}-1$ and $F(T)$ are given in the annexed tables for any value of T and, putting $T=T_a$, the following values for $\frac{1}{P}\frac{dP}{dT}$ are obtained in the cases of Pentane, Hexane, Heptane, Octane, Decane, and Nonadecane.

Pentane	$\frac{1}{P}\frac{dP}{dT}=0{\cdot}033255$
Hexane	$=0{\cdot}030801$
Heptane	$=0{\cdot}028887$
Octane	$=0{\cdot}027347$
Decane	$=0{\cdot}025113$
Nonadecane	$=0{\cdot}020510$

From the Clapeyron equation we have

$$\frac{dP}{dT}=\frac{L}{V-V_0\,T}$$

and $V-V_0$ is very nearly equal to V in the case of all the hydrocarbons under consideration. For all practical purposes it may be taken as equal to 0·995 V. Further the general gas equation, PV=R.T, is approximately true at the boiling point of the oils when the boiling point is sufficiently far removed from the critical temperature. If we write $PV=R^1.T$ where R^1 is a little less than R, the Clapeyron equation becomes

$$\frac{dP}{dT}=\frac{P.L}{0{\cdot}995\ R^1.T^2}$$

or

$$\frac{1}{P}\frac{dP}{dT}=\frac{L}{0{\cdot}995\ R^1.T^2}$$

From this the following values of the molal latent heats of the above hydrocarbons are obtained :

Pentane	$L=0{\cdot}995\ R^1\times309{\cdot}3^2\times0{\cdot}033255=R^1.\ 3{,}165$
Hexane	$L=0{\cdot}995\ R^1\times342{\cdot}0^2\times0{\cdot}030801=R^1.\ 3{,}585$
Heptane	$L=0{\cdot}995\ R^1\times371{\cdot}4^2\times0{\cdot}028887=R^1.\ 3{,}964$
Octane	$L=0{\cdot}995\ R^1\times398{\cdot}8^2\times0{\cdot}027347=R^1.\ 4{,}328$
Decane	$L=0{\cdot}995\ R^1\times446{\cdot}6^2\times0.025113=R^1.\ 4{,}971$
Nonadecane	$L=0{\cdot}995\ R^1\times603{\cdot}0^2\times0{\cdot}020510=R^1.\ 7{,}421$

Experimental observations have been made on the latent heats of the first five of the above hydrocarbons. Comparing these with the figures obtained by dividing the above figures by the molecular weights, the following values of R^1 are obtained :

	Calculated Latent Heat.	Observed Latent Heat.	R^1.
Pentane	$R^1\times43{\cdot}96$ ..	85·8 ..	1·952
Hexane	$R^1\times41{\cdot}69$ ..	79·2 ..	1·900
Heptane	$R^1\times39{\cdot}64$ ..	74·0 ..	1·867
Octane	$R^1\times37{\cdot}96$ ..	71·1 ..	1·873
Decane	$R^1\times35{\cdot}01$ ..	61·0 ..	1·742

The value of R^1 seems to diminish regularly except in the case of Octane, of which the observed latent heat seems to be too high. Comparing R^1 with the gas constant R=1·9855, the ratio of R^1/R is in the case of Pentane, 98·3 per cent. ; of Hexane, 95·7 per cent. ; of Heptane, 94·0 per cent. ; of Octane, 94·3 per cent. ; and of Decane, 87·7 per cent. It would hardly be expected that the

higher members of the series would vary more from the perfect gas laws than the lower, as their boiling points would presumably be farther removed from the critical temperatures.

In the case of Nonadecane there is no direct observation of the latent heat with which to compare the calculated value. We have, however, von Trouton's equation as modified by Nernst as a means of comparison. This equation is

$$L/T = 9{\cdot}5 \log_{10} T - 0{\cdot}007T.$$

Giving T its observed value of 603, we have

$$L = 13{,}380.$$

Comparing this with the calculated value given above of $R^1 \times 7421$, we get $R^1 = 1{\cdot}803$, which has a ratio R^1/R of 90·8 per cent.

This ratio is again too low when the relation of the boiling point to the probable critical temperature is considered, but is too high when considered as one of a descending values as evidenced from the values of the ratio R^1/R in the cases of Pentane, Hexane, Heptane and Decane. This development of a fairly accurate law for the variation of the vapour tensions of the normal paraffins with their boiling points seems to show that considerable doubt may be held as to the accuracy of the few observed latent heats and the latent heats as deduced from von Trouton's law, even as modified by Nernst.

TABLE OF VALUES FOR EMPIRICAL FORMULA FOR VAPOUR TENSIONS OF PETROLEUMS.

t. = Temperature Centigrade.
$F(T) = (T^2 + A^2)^{\frac{1}{2}} - h$.

T. = Absolute Temperature.
Expression = 1,250/F(T) — 1.

t.	T.	F(T).	Exprn.	t.	T.	F(T).	Exprn.
—40	233	95·25	12·122	—21	252	106·53	10·735
—39	234	95·83	12·043	—20	253	107·14	10·669
—38	235	96·41	11·967	—19	254	107·75	10·601
—37	236	96·99	11·888	—18	255	108·36	10·536
—36	237	97·58	11·811	—17	256	108·97	10·470
—35	238	98·16	11·733	—16	257	109·59	10·406
—34	239	98·75	11·659	—15	258	110·21	10·342
—33	240	99·34	11·581	—14	259	110·82	10·280
—32	241	99·93	11·509	—13	260	111·45	10·218
—31	242	100·52	11·433	—12	261	112·06	10·157
—30	243	101·12	11·363	—11	262	112·69	10·094
—29	244	101·71	11·291	—10	263	113·31	10·031
—28	245	102·31	11·219	— 9	264	113·94	9·970
—27	246	102·91	11·148	— 8	265	114·56	9·911
—26	247	103·51	11·077	— 7	266	115·19	9·852
—25	248	104·11	11·007	— 6	267	115·82	9·793
—24	249	104·71	10·937	— 5	268	116·45	9·735
—23	250	105·32	10·869	— 4	269	117·08	9·678
—22	251	105·92	10·801	— 3	270	117·72	9·619

t.	T.	F(T).	Exprn.
— 2	271	118·36	9·562
— 1	272	118·99	9·514
0	273	119·63	9·448
1	274	120·27	9·394
2	275	120·91	9·339
3	276	121·55	9·284
4	277	122·20	9·231
5	278	122·84	9·176
6	279	123·49	9·123
7	280	124·14	9·070
8	281	124·79	9·017
9	282	125·44	8·964
10	283	126·09	8·914
11	284	126·74	8·862
12	285	127·40	8·812
13	286	128·05	8·762
14	287	128·71	8·712
15	288	129·37	8·662
16	289	130·02	8·614
17	290	130·69	8·565
18	291	131·35	8·516
19	292	132·01	8·468
20	293	132·68	8·421
21	294	133·35	8·374
22	295	134·01	8·328
23	296	134·68	8·281
24	297	135·35	8·374
25	298	136·02	8·190
26	299	136·69	8·145
27	300	137·37	8·099
28	301	138·04	8·055
29	302	138·72	8·011
30	303	139·40	7·967
31	304	140·07	7·924
32	305	140·75	7·881
33	306	141·43	7·839
34	307	142·11	7·796
35	308	142·80	7·754
36	309	143·48	7·712
37	310	144·17	7·671
38	311	144·85	7·629
39	312	145·54	7·588
40	313	146·24	7·548
41	314	146·92	7·508
42	315	147·61	7·468
43	316	148·30	7·428
44	317	149·00	7·390
45	318	149·69	7·351
46	319	150·39	7·312
47	320	151·09	7·273
48	321	151·78	7·234
49	322	152·49	7·198
50	323	153·19	7·160
51	324	153·89	7·123
52	325	154·59	7·086
53	326	155·29	7·050
54	327	155·99	7·013
55	328	156·70	6·977
56	329	157·41	6·940
57	330	158·12	6·905
58	331	158·83	6·869
59	332	159·54	6·834
60	333	160·26	6·800
61	334	160·97	6·766
62	335	161·68	6·731
63	336	162·40	6·697
64	337	163·11	6·663
65	338	163·83	6·629
66	339	164·54	6·596
67	340	165·26	6·564
68	341	165·98	6·531
69	342	166·70	6·498
70	343	167·42	6·466
71	344	168·15	6·434
72	345	168·87	6·403
73	346	169·59	6·371
74	347	170·32	6·339
75	348	171·05	6·308
76	349	171·77	6·277
77	350	172·50	6·246
78	351	173·23	6·216
79	352	173·96	6·185
80	353	174·69	6·155
81	354	175·43	6·125
82	355	176·16	6·096
83	356	176·89	6·067
84	357	177·65	6·037
85	358	178·36	6·008
86	359	179·10	5·980
87	360	179·84	5·950
88	361	180·58	5·922
89	362	181·32	5·893
90	363	182·06	5·866
91	364	182·80	5·838
92	365	183·54	5·810
93	366	184·29	5·783
94	367	185·03	5·756
95	368	185·78	5·728
96	369	186·52	5·702
97	370	187·27	5·675
98	371	188·02	5·648
99	372	188·77	5·622
100	373	189·52	5·595
101	374	190·27	5·569
102	375	191·02	5·543
103	376	191·77	5·519
104	377	192·53	5·492
105	378	193·28	5·467
106	379	194·04	5·422
107	380	194·79	5·417
108	381	195·55	5·392
109	382	196·31	5·367
110	383	197·07	5·343
111	384	197·83	5·318
112	385	198·58	5·294
113	386	199·34	5·270
114	387	200·11	5·246
115	388	200·87	5·223
116	389	201·63	5·199
117	390	202·40	5·176

t.	T.	F(T).	Exprn.
118	391	203·16	5·153
119	392	203·93	5·130
120	393	204·70	5·107
121	394	205·46	5·084
122	395	206·23	5·061
123	396	207·00	5·039
124	397	207·77	5·016
125	398	208·54	4·993
126	399	209·31	4·972
127	400	210·08	4·950
128	401	210·86	4·928
129	402	211·63	4·906
130	403	212·41	4·885
131	404	213·18	4·864
132	405	213·96	4·843
133	406	214·73	4·821
134	407	215·51	4·800
135	408	216·29	4·779
136	409	217·07	4·758
137	410	217·85	4·738
138	411	218·63	4·717
139	412	219·41	4·697
140	413	220·20	4·677
141	414	220·98	4·657
142	415	221·76	4·637
143	416	222·54	4·617
144	417	223·33	4·597
145	418	224·11	4·577
146	419	224·90	4·558
147	420	225·69	4·539
148	421	226·48	4·519
149	422	227·26	4·500
150	423	228·06	4·480
151	424	228·84	4·462
152	425	229·63	4·443
153	426	230·42	4·424
154	427	231·22	4·406
155	428	232·01	4·388
156	429	232·80	4·369
157	430	233·60	4·351
158	431	234·39	4·333
159	432	235·19	4·315
160	433	235·99	4·297
161	434	236·78	4·279
162	435	237·58	4·262
163	436	238·38	4·243
164	437	239·17	4·226
165	438	239·97	4·209
166	439	240·77	4·192
167	440	241·57	4·175
168	441	242·38	4·157
169	442	243·18	4·410
170	443	243·99	4·124
171	444	244·79	4·107
172	445	245·59	4·090
173	446	246·39	4·074
174	447	247·20	4·057
175	448	248·00	4·040
176	449	248·81	4·024
177	450	249·62	4 007

t.	T.	F(T).	Exprn.
178	451	250·43	3·991
179	452	251·24	3·975
180	453	252·05	3·959
181	454	252·86	3·943
182	455	253·67	3·928
183	456	254·47	3·912
184	457	255·28	3·896
185	458	256·10	3·881
186	459	256·91	3·866
187	460	257·72	3·850
188	461	258·54	3·835
189	462	259·36	3 820
190	463	260·17	3·804
191	464	260·99	3·789
192	465	261·80	3·774
193	466	262·62	3·759
194	467	263·43	3·744
195	468	264·25	3·730
196	469	265·07	3·716
197	470	265·99	3·700
198	471	266·71	3·686
199	472	267·53	3·672
200	473	268·36	3·658
201	474	269·18	3·644
202	475	270·00	3·630
203	476	270·82	3·615
204	477	271·64	3·601
205	478	272·46	3·587
206	479	273·29	3·574
207	480	274·11	3·560
208	481	274·94	3·546
209	482	275·77	3·533
210	483	276·60	3·519
211	484	277·43	3·506
212	485	278·25	3·494
213	486	279·08	3·479
214	487	279·91	3·466
215	488	280·74	3·453
216	489	281·57	3·439
217	490	282·40	3·426
218	491	283·23	3·413
219	492	284·06	3·400
220	493	284·89	3·387
221	494	285·73	3·374
222	495	286·56	3·362
223	496	287·39	3·349
224	497	288·23	3·336
225	498	289·06	3·324
226	499	289·89	3·312
227	500	290·73	3·299
228	501	291·57	3·287
229	502	292·40	3·275
230	503	293·24	3·263
231	504	294·08	3·251
232	505	294·91	3·239
233	506	295·75	3·227
234	507	296·59	3·215
235	508	297·43	3·203
236	509	298·27	3·191
237	510	299·11	3·179

t.	T.	F(T).	Exprn.
238	511	299·95	3·167
239	512	300·79	3·156
240	513	301·64	3·144
241	514	302·48	3·132
242	515	303·32	3·121
243	516	304·16	3·110
244	517	305·01	3·098
245	518	305·85	3·087
246	519	306·70	3·076
247	520	307·54	3·065
248	521	308·39	3·054
249	522	309·23	3·042
250	523	310·08	3·031
251	524	310·93	3·020
252	525	311·77	3·009
253	526	312·62	2·998
254	527	313·47	2·987
255	528	314·32	2·976
256	529	315·17	2·966
257	530	316·02	2·955
258	531	316·87	2·945
259	532	317·72	2·934
260	533	318·57	2·924
261	534	319·42	2·913
262	535	320·27	2·903
263	536	321·12	2·893
264	537	321·98	2·883
265	538	322·83	2·872
266	539	323·68	2·862
267	540	324·54	2·852
268	541	325·39	2·842
269	542	326·25	2·831
270	543	327·10	2·821
271	544	327·96	2·811
272	545	328·81	2·801
273	546	329·67	2·791
274	547	330·53	2·781
275	548	331·38	2·772
276	549	332·24	2·762
277	550	333·10	2·753
278	551	333·96	2·743
279	552	334·82	2·733
280	553	335·68	2·724
281	554	336·54	2·714
282	555	337·40	2·705
283	556	338·26	2·695
284	557	339·12	2·686
285	558	339·98	2·677
286	559	340·84	2·667
287	560	341·71	2·658
288	561	342·57	2·649
289	562	343·43	2·639
290	563	344·30	2·630
291	564	345·16	2·621
292	565	346·02	2·612
293	566	346·89	2·603
294	567	347·75	2·594
295	568	348·62	2·585
296	569	349·48	2·577
297	570	350·35	2·568
298	571	351·22	2·559
299	572	352·08	2·550
300	573	352·95	2·542
301	574	353·82	2·533
302	575	354·69	2·524
303	576	355·55	2·516
304	577	356·42	2·507
305	578	357·29	2·499
306	579	358·16	2·490
307	580	359·03	2·481
308	581	359·90	2·473
309	582	360·77	2·465
310	583	361·64	2·456
311	584	362·51	2·448
312	585	363·39	2·440
313	586	364·26	2·431
314	587	365·13	2·423
315	588	366·00	2·415
316	589	366·88	2·407
317	590	367·75	2·399
318	591	368·64	2·391
319	592	369·50	2·383
320	593	370·37	2·375
321	594	371·25	2·367
322	595	372·12	2·359
323	596	373·00	2·351
324	597	373·88	2·407
325	598	374·75	2·335
326	599	375·63	2·328
327	600	376·50	2·320
328	601	377·38	2·312
329	602	378·26	2·304
330	603	379·14	2·297
331	604	380·02	2·289
332	605	380·89	2·282
333	606	381·77	2·274
334	607	382·65	2·267
335	608	383·53	2·259
336	609	384·41	2·252
337	610	385·29	2·244
338	611	386·17	2·237
339	612	287·05	2·230
340	613	387·93	2·222
341	614	388·82	2·215
342	615	389·70	2·208
343	616	390·58	2·200
344	617	391·46	2·193
345	618	392·35	2·186
346	619	393·23	2·179
347	620	394·11	2·171
348	621	395·00	2·164
349	622	395·88	2·157
350	623	396·76	2·150
351	624	397·65	2·143
352	625	398·53	2·136
353	626	399·42	2·129
354	627	400·30	2·122
355	628	401·19	2·115
356	629	402·08	2·109
357	630	402·96	2·102
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t.	T.	F(T).	Exprn.	t.	T.	F(T).	Exprn.
358	631	403·85	2·095	418	691	457·57	1·731
359	632	404·74	2·088	419	692	458·47	1·726
360	633	405·62	2·082	420	693	459·37	1·721
361	634	406·51	2·075	421	694	460·28	1·716
362	635	407·40	2·068	422	695	461·18	1·710
363	636	408·29	2·062	423	696	462·09	1·705
364	637	409·18	2·055	424	697	462·99	1·700
365	638	410·07	2·048	425	698	463·89	1·695
366	639	410·95	2·042	426	699	464·80	1·689
367	640	411·84	2·035	427	700	465·70	1 684
368	641	412·73	2·028	428	701	466·61	1·679
369	642	413·62	2·022	429	702	467·51	1·674
370	643	414·51	2·015	430	703	468·42	1·668
371	644	415·40	2·009	431	704	469·33	1·663
372	645	416·30	2·002	432	705	470·23	1·658
373	646	417·19	1·996	433	706	471·14	1·653
374	647	418 08	1·989	434	707	472·05	1·648
375	648	418·97	1·983	435	708	472·95	1·643
376	649	419·86	1·977	436	709	473·86	1·638
377	650	420·75	1·970	437	710	474·77	1·633
378	651	421·65	1·964	438	711	475·68	1·628
379	652	422·54	1·958	439	712	476·58	1·623
380	653	423·43	1·952	440	713	477·49	1·618
381	654	424·33	1·946	441	714	478·40	1·613
382	655	425·22	1·940	442	715	479·31	1·608
383	656	426·11	1·934	443	716	480·22	1·603
384	657	427·01	1·927	444	717	481·13	1·598
385	658	427·90	1·921	445	718	482·03	1·593
386	659	428·80	1·915	446	719	482·94	1·588
387	660	429·59	1·909	447	720	483·85	1·584
388	661	430·49	1·903	448	721	484·76	1·579
389	662	431·38	1·899	449	722	485·67	1·574
390	663	432·38	1·891	450	723	486·58	1·569
391	664	433·27	1·885	451	724	487·49	1·564
392	665	434·17	1·879	452	725	488·41	1·559
393	666	435·07	1·873	453	726	489·32	1·555
394	667	435·97	1·867	454	727	490·23	1·550
395	668	436·86	1·861	455	728	491 14	1·545
396	669	437·76	1·855	456	729	492·05	1·540
397	670	438·66	1·849	457	730	492·96	1·536
398	671	439·56	1·844	458	731	493·87	1·531
399	672	440·45	1·838	459	732	494·79	1·526
400	673	441·35	1·832	460	733	495·70	1·521
401	674	442·25	1·826	461	734	496 61	1·517
402	675	443·15	1·821	462	735	497·52	1·512
403	676	444·05	1 815	463	736	498·44	1·508
404	677	444·95	1·810	464	737	499·35	1·503
405	678	445·85	1·804	465	738	500·26	1·498
406	679	446·75	1·798	466	739	501·18	1·494
407	680	447·65	1·792	467	740	502·09	1·489
408	681	448·55	1·787	468	741	503·01	1·485
409	682	449·45	1·781	469	742	503·92	1·480
410	683	450·35	1·776	470	743	504·83	1·476
411	684	451 25	1 770	471	744	505·75	1·471
412	685	452·15	1·764	472	745	506·66	1·467
413	686	453·05	1·759	473	746	507·58	1·462
414	687	453·95	1·753	474	747	508·49	1·458
415	688	454·86	1·748	475	748	509·41	1·453
416	689	455·76	1·742	476	749	510·32	1·449
417	690	456·66	1·737	477	750	511·24	1·445

t.	T.	F(T).	Exprn.	t.	T.	F(T).	Exprn.
478	751	512·16	1·440	490	763	523·16	1·389
479	752	513·07	1·436	491	764	524·08	1·385
480	753	513·99	1·432	492	765	525·00	1·381
481	754	514·91	1·428	493	766	525·92	1·377
482	755	515·82	1·423	494	767	526·84	1·373
483	756	516·74	1·419	495	768	527·76	1·368
484	757	517·66	1·415	496	769	528·68	1·364
485	758	518·57	1·411	497	770	529·60	1·360
486	759	519·49	1·406	498	771	530·52	1·356
487	760	520·41	1·402	499	772	531·44	1·352
488	761	521·33	1·397	500	773	532·36	1·348
489	762	522·25	1·393				

VAPOUR TENSIONS OF PETROLEUMS. OBSERVED AND CALCULATED BOILING POINTS.

Hydrocarbon.		B.P. at 760 mm.	B.P. at 100 mm.	B.P. at 50 mm.	B.P. at 30 mm.	B.P. at 20 mm.	B.P. at 10 mm.	B.P. at 5 mm.
Normal Paraffins.								
Pentane	Obs.	36·3	—13·2	—26·1				
C_5H_{12}	Cal.		—13·1	—26·3				
	Dif.		+ 0·1	— 0·2				
Hexane	Obs.	69·0	15·6	1·5	— 7·9	—15·0	—25·7	—34·1
C_6H_{14}	Cal.		15·6	1·5	— 7·8	—14·8	—25·7	—35·7
	Dif.		0·0	0·0	+ 0·1	+ 0·2	0·0	— 1·6
Heptane	Obs.	98·4	41·6	26·4	16·3	9·5	— 2·1	
C_7H_{16}	Cal.		41·4	26·4	16·4	9·0	— 2·7	
	Dif.		— 0·2	0·0	+ 0·1	— 0·5	— 0·6	
Octane	Obs.	125·8	65·6	50·2	39·3	31·3	19·1	7·7
C_8H_{18}	Cal.		65·5	50·7	39·1	30·7	19·0	7·8
	Dif.		— 0·1	+ 0·5	— 0·2	— 0·6	— 0·1	+ 0·1
Nonane	Obs.	149·5	86·0	70·0	59·0	49·0	38·0	
C_9H_{20}	Cal.		86·5	69·9	59·2	50·6	37·7	
	Dif.		+ 0·5	— 0·1	+ 0·2	+ 1·6	— 0·3	
Decane	Obs.	173·0	107·0	90·0	78·0	68·0	55·0	
$C_{10}H_{22}$	Cal.		107·2	89·8	78·2	69·7	56·2	
	Dif.		+ 0·2	— 0·2	+ 0·2	+ 1·7	+ 1·2	
Undecane ..	Obs.	194·5	127·0	108·5	96·5	87·0	72·0	
$C_{11}H_{24}$	Cal.		126·3	108·3	96·3	87·3	73·3	
	Dif.		— 0·7	— 0·2	— 0·2	+ 0·3	+ 1·3	
Dodecane ..	Obs.	214·5	145·5	126·0	113·8	103·0	88·0	
$C_{12}H_{26}$	Cal.		144·0	125·4	112·9	103·7	89·2	
	Dif.		— 1·5	— 0·6	— 0·9	+ 0·7	+ 1·2	
Tridecane ..	Obs.	234·0	162·5	142·5	130·0	120·0	106·0	
$C_{13}H_{28}$	Cal.		161·3	142·2	129·3	119·8	104·8	
	Dif.		— 1·2	— 0·3	— 0·7	— 0·2	— 1·2	
Tetradecane ..	Obs.	252·5	178·5	158·0	145·5	136·0	121·0	
$C_{14}H_{30}$	Cal.		178·0	158·3	145·0	135·2	119·8	
	Dif.		— 0·5	+ 0·3	— 0·5	— 0·8	— 1·2	
Pentadecane ..	Obs.	270·5	194·0	173·0	160·0	150·0	135·0	
$C_{15}H_{32}$	Cal.		194·1	173·9	160·3	150·2	134·4	
	Dif.		+ 0·1	+ 0·9	+ 0·3	+ 0·2	— 0·6	
Hexadecane ..	Obs.	287·5	208·5	187·5	174·0	165·0	149·0	
$C_{16}H_{34}$	Cal.		209·5	188·7	174·6	164·4	148·3	
	Dif.		+ 1·0	+ 1·2	+ 0·6	— 0·6	— 0·7	

Hydrocarbon.		B.P. at 760 mm.	B.P. at 100 mm.	B.P. at 50 mm.	B.P. at 30 mm.	B.P. at 20 mm.	B.P. at 10 mm.	B.P. at 5 mm.
Heptadecane ..	Obs.	303·0	223·0	201·5	187·5	177·0	161·0	
$C_{17}H_{36}$	Cal.		223·4	202·2	188·0	177·4	160·8	
	Dif.		+ 0·4	+ 0·7	+ 0·5	+ 0·4	— 0·2	
Octadecane ..	Obs.	317·0		214·5	200·0	189·0	172·0	
$C_{18}H_{38}$	Cal.		236·2	214·7	199·9	189·4	172·4	
	Dif.			+ 0·2	— 0·1	+ 0·4	+ 0·4	
Nonadecane ..	Obs.	330·0	248·0	226·5	212·0	200·0	183·0	
$C_{19}H_{40}$	Cal.		248·1	226·2	211·3	200·5	183·1	
	Dif.		+ 0·1	— 0·3	— 0·7	+ 0·5	+ 0·1	
Heneicosan ..	Obs.	358·0				224·0	205·0	
$C_{21}H_{44}$	Cal.					224·5	206·6	
	Dif.					+ 0·5	+ 1·6	
Docosan	Obs.	370·0 (about)				232·0	213·0	
$C_{22}H_{46}$	Cal.					235·0	216·8	
	Dif.					+ 3·0	+ 3·8	
Tricosan ..	Obs.	383·0 (about)				242·0	223·0	
$C_{23}H_{48}$	Cal.					246·2	227·6	
	Dif.					+ 4·2	+ 4·6	
Tetracosan ..	Obs.	395·0 (about)					231·0	
$C_{24}H_{50}$	Cal.						238·0	
	Dif.						+ 7·0	
Dotriacontane ..	Obs.	485·0 (about)					310·5	
$C_{32}H_{66}$	Cal.						316·0	
	Dif.						+ 5·5	
Iso-Paraffins.								
Iso-Pentane ..	Obs.	27·9	—20·0	—32·0				
C_5H_{12}	Cal.		—20·4	—33·4				
	Dif.		— 0·4	— 1·4				
Diiso-Propyl ..	Obs.	58·1	4·6	— 8·6				
C_6H_{14}	Cal.		6·0	— 7·7				
	Dif.		+ 1·6	+ 0·9				
Diiso-Butyl ..	Obs.	109·2	50·8	34·9	24·5	16·9	5·7	— 6·0
C_8H_{18}	Cal.		51·0	35·7	25·4	17·8	5·9	— 4·9
	Dif.		+ 0·2	+ 0·8	+ 0·9	+ 0·9	+ 0·2	+ 1·1
Aromatics.								
Benzene	Obs.	80·2	25·8	11·6	1·8	— 4·3	—13·6	—22·1
C_6H_6	Cal.		25·4	11·0	1·4	— 6·3	—17·0	—27·1
	Dif.		— 0·4	— 0·6	— 0·4	— 2·0	— 3·4	— 5·0
Toluene	Obs.	110·4	51·8	36·3	25·5	17·9	6·0	
$C_6H_5CH_3$	Cal.		52·0	36·7	26·4	18·8	6·6	
	Dif.		+ 0·2	+ 0·4	+ 0·9	+ 0·9	+ 0·6	
Ethyl Benzene ..	Obs.	136·6	74·2	57·4	46·2		30·0	
$C_6H_5C_2H_5$	Cal.		75·0	58·8	48·0		27·5	
	Dif.		+ 0·8	+ 1·4	+ 1·8		— 2·5	
p-Xylene ..	Obs.	138·9	76·4	59·5	48·0			
$C_6H_4(CH_3)_2$	Cal.		77·1	60·9	50·0			
	Dif.		+ 0·7	+ 1·4	+ 2·0			
m-Xylene ..	Obs.	139·5	76·9	60·2	49·1		30·0	
$C_6H_4(CH_3)_2$	Cal.		77·6	61·3	50·5		29·8	
	Dif.		+ 0·7	+ 1·1	+ 1·4		— 0·2	
o-Xylene	Obs.	144·0	81·2	64·1	52·6	44·5		
$C_6H_4(CH_3)_2$	Cal.		81·6	65·1	54·2	46·1		
	Dif.		+ 0·4	+ 1·0	+ 1·6	+ 1·6		
Isopropyl Benzene	Obs.	155·1	90·1	72·5	60·8	52·0		
$C_6H_5CH(CH_3)_2$	Cal.		91·4	74·6	63·4	55·1		
	Dif.		+ 1·3	+ 2·1	+ 2·6	+ 3·1		

Hydrocarbon.		B.P. at 760 mm.	B.P. at 100 mm.	B.P. at 50 mm.	B.P. at 30 mm.	B.P. at 20 mm.	B.P. at 10 mm.	B.P. at 5 mm.
n-Propyl Benzene	Obs.	158·8				57·0	45·0	
$C_6H_5C_3H_7$	Cal.					58·1	45·0	
	Dif.					+ 1·1	0·0	
p-Ethyl Toluene	Obs.	162·0					46·0	
$C_6H_4(C_2H_5)CH_3$	Cal.						47·5	
	Dif.						+ 1·5	
Mesitylene ..	Obs.	164·5					49·0	
$C_6H_3(CH_3)_3$	Cal.						49·5	
	Dif.						+ 0·5	
p-Cymole ..	Obs.	174·3					57·0	
$C_6H_4(C_3H_7)CH_3$	Cal.						57·3	
	Dif.						+ 0·3	
*(Naphthaline)								
Heptyl Benzene ..	Obs.	233·0					108·0	
$C_6H_5C_7H_{15}$	Cal.						104·0	
	Dif.						— 4·0	
Diphenyl ..	Obs.	254·0					117·0	
$(C_6H_5)_2$	Cal.						121·0	
	Dif.						+ 4·0	
*Naphthaline ..	Obs.	218·1		125·8	112·6	101·9	86·9	75·0
$C_{10}H_8$	Cal.			128·5	116·0	106·1	92·1	78·8
	Dif.			+ 2·7	+ 3·4	+ 4·2	+ 5·2	+ 3·8
Caryophyllene ..	Obs.	260·0					120·0	
$C_{15}H_{24}$	Cal.						125·8	
	Dif.						+ 5·8	
Cadinene	Obs.	274·0						131·0
$C_{15}H_{24}$	Cal.							122·7
	Dif.							— 8·3
* Anthracene.								
Ethylenes.								
Hexamethylene ..	Obs.	80·9	25·2	11·0	1·3			
C_6H_{12} (cyclic)	Cal.		26·1	11·8	2·0			
	Dif.		+ 0·9	+ 0·8	+ 0·7			
Oxtylene	Obs.	123·0				31·0	19·0	
C_8H_{16}	Cal.					29·0	16·7	
	Dif.					— 2·0	— 2·3	
Decylene	Obs.	172·0	107·0	88·0		68·0	54·0	
$CH_3CH(CH_2)_7CH_2$	Cal.		105·7	89·0		68·9	55·4	
	Dif.		— 1·3	+ 1·0		+ 0·9	+ 1·4	
Dodecylene ..	Obs.	208·0				102·0	89·0	
$CH_3CH(CH_2)_9CH_2$	Cal.					98·4	84·0	
	Dif.					— 3·6	— 5·0	
Tetradecylene ..	Obs.	243·0				133·0	120·0	
$CH_3CH(CH_2)_{11}CH_2$	Cal.					127·3	112·0	
	Dif.					— 5·7	— 8·0	
Hexadecylene ..	Obs.	274·0				161·0	144·0	
$CH_3CH(CH_2)_{13}CH_2$	Cal.					153·2	137·2	
	Dif.					— 7·8	— 6·8	
*Anthracene ..	Obs.	351·0	250·2	224·7	206·9	194·4	174·7	158·5
$(C_6H_4CH)_2$	Cal.		267·5	244·9	229·7	218·5	200·8	184·5
	Dif.		+17·3	+20·2	+22·8	+24·1	+26·1	+26·0

Natural Gas in 1923.

By S. J. M. Auld, O.B.E. M.C., D.Sc.

The exploitation of natural gas continues to grow from year to year, and there is now little occurring natural gas which is not harnessed and utilised in some way or another. In the United States of America the bulk of the gas is available as fuel for industrial and domestic purposes, and its adaptability and general value as a fuel have caused most of the gas-producing States to pass laws limiting or altogether prohibiting its use in more wasteful processes, such as the production of carbon black.

Natural gas is of two kinds, "wet" and "dry." The former carries appreciable quantities of condensable hydrocarbons and accompanies oil or comes from oil-bearing strata, whereas the latter generally occurs in sands entirely separated from strata containing oil. Casing-head gas is, of course, wet. There is, however, no sharp line of demarcation between the two varieties, and much natural gas hitherto classified as dry is now actually being used as a source of gasoline.

The hydrocarbons of natural gas are almost wholly paraffinoid in character and preponderatingly methane. Some gases, notably certain Kansas gases, contain large amounts of nitrogen, and the natural gas of Southern Persia contains over 10 per cent. of sulphuretted hydrogen; but these are exceptions. It is significant that more and more attention is being paid to the possibility of using natural gas hydrocarbons as a source of new products, but in the meantime their utilisation generally proceeds along the following lines:—

(1) The gas is stripped of its condensable hydrocarbons.

(2) The residual gas is

  (*a*) Used for the production of carbon black or of hard carbon;

  (*b*) Burnt as fuel.

Natural Gas Gasoline.

At present practically the whole of the world's natural gasoline comes from the U.S.A., and according to the latest official reports[1] there were produced 506,000,000 gallons in 1922, this being an increase of 13 per cent. over 1921, and approximately 500 per cent. over the 1916 output.

[1] *U.S. Geol. Survey*, 1922.

The natural gasoline output of America is approximately 8 per cent. of that obtained by distillation of crude petroleum. Since the market value relative to straight run gasoline has consistently kept pace with the production, it is obvious that the natural gasoline industry is a highly important branch of the motor fuel trade. In point of fact its advent has made possible the extended use of naphtha and other blending products, otherwise unsaleable as motor spirit, and has permitted the efficient production of blended gasolines of any required specific gravity and boiling range.

Like the general petroleum industry, the natural gasoline industry has just passed through a period of depression due to over-production, but the prospects for the coming years are good, and H. J. Struth[2] indicates that the maximum yields of natural gasoline will be readily absorbed by the motor spirit market.

There have been many important developments in the stripping of gasoline from natural gas, the most noteworthy being the extent to which poor gases are being treated, generally by a combination of the absorption and compression processes. According to I. R. C. Cantelo[3] gases containing as little as a quart of recoverable gasoline per 1000 cub. ft. are being successfully worked, and this is by no means the lowest. In handling lean gases of this type large throughputs are necessary if the operation of extraction is to be profitable, and E. G. Sievers[4] states that in America the majority of the small plants are being consolidated as it is scarcely profitable to produce less than 1000 gallons of gasoline per day in a single plant.

Another development of great importance is the extent to which absorption practice at low pressure is being applied to the richer casing-head gases. These gases in the past were almost invariably treated by compression and refrigeration methods, but casing-head gasoline is notoriously "wild," and the growing reluctance of many purchasers to accept blended spirits of this kind has led to the adoption of absorption processes operated at little more than atmospheric pressure. The results have been eminently satisfactory, and this method is gradually ousting the more costly compression process. Absorption process casing-head gasoline has such a vapour pressure that blending is not actually necessary, though generally resorted to. The comparatively low vapour pressure is due to selective absorption in the first place and to automatic "weathering" during the subsequent distillation in the second. The design and operation of a low-pressure

[2] *Oil Trade J.*, 1924, **15**, 4, 68.
[3] *Canad. Chem. and Met.*, 1922, **6**, 177, 196.
[4] *Chem. Met. Eng.*, 1923, **28**, 297.

absorption plant has been described by W. P. Dykema and A. A. Chenoweth[5] of the U.S. Bureau of Mines.

During 1922 absorption methods had increased 74 per cent. in the U.S.A., compression methods decreased 10 per cent., and combination plants increased 29 per cent. over 1921.[6]

The method devised by G. Burrell[7] for stripping gasoline from natural gas by passing it through activated charcoal is finding a firm footing in the industry. The process is very selective and can be made to effect very sharp separation of the condensable gasoline from the other constituents. It appears to be particularly applicable to the treatment of lean natural gases and the further treatment of residual gas from compression and low-pressure absorption processes, and the charcoal process is now frequently installed in this way to effect additional stripping.[8] W. Friedmann[9] and Meister, Lucius and Brüning[10] have devised continuous plant for the charcoal process, avoiding the need of segregating a section or removing the charcoal for revivification.

In a portable form of apparatus activated charcoal is frequently used for measuring the gasoline content of natural gas, but the figures obtained are not strictly comparable with those from absorption in gas oil. In this connection the Gasoline Committee of the Natural Gas Association of America has made a preliminary report[11] on their attempts to standardise the efficiency and meaning of such tests. This is badly needed owing to the indiscriminate use of the term "natural gasoline" to cover both the wildest and most stable products.

R. P. Anderson and A. M. Erskine[12] give an account of the actual composition of natural gasoline, which should be consulted by those interested.

The obvious advantages attending the removal of the most volatile constituents of natural gasoline, generally effected by the wasteful method of "weathering," have led to the development by J. A. Rafferty[13] of a stabilising apparatus which separates all the gaseous constituents and leaves in the finished product only such liquid fractions as may be desired. The plant is, in effect, a fractionating column working at low temperatures, and, in the case of compression gasoline, obtaining added effect by the refrigeration caused by evaporation on

[5] *Bureau Mines Tech. Paper* 263, 1922.
[6] *Chem. and Met. Eng.*, 1921, **24**, 4.
[7] *Cf. Nat. Petr. News*, 1924, **16**, 5.
[8] *Refiner*, 1923, **2**, 11, 7.
[9] *Petroleum*, 1923, **19**, 367.
[10] Eng. Pat. 187,223.
[11] *Oil Trade J.*, 1924, **15**, 62.
[12] *Ind. Eng. Chem.*, 1924, **16**, 262.
[13] *Nat. Petr. News*, 1923, **15**, 17.

expansion of the lightest fractions. Results obtained by L. F. Baker,[14] of the Tidal Refining Company, one of the licensees of the process, lead one to believe that the "stabiliser" is one of the most important contributions to the manufacture of natural gasoline since the adoption of the absorption process.

The natural gasoline from some gases tends rapidly to go off colour and become "sour," and D. B. Dow[15], in a description of known methods of purifying this gasoline, lays considerable stress on the value of the caustic soda solution of litharge generally known as "doctor" solution.

Carbon Black.

The manufacture of carbon black by the limited combustion of natural gas is a very important industry, especially in the U.S.A., whence practically the whole of the world's supplies come. According to a compilation by G. B. Richardson[16] nearly 68,000,000 lbs. of carbon black were produced in 1922, this being 13 per cent. more than the 1921 output. Louisiana and West Virginia produced more than 90 per cent. of the total. The average price obtained for the year was 8·6 cents per lb. at the plant.

As mentioned above, the use of natural gas for making carbon black has been strongly deprecated, and in many industrial districts its employment in this way has been vetoed. The yield of black varies from 0·8 lb. to 1·4 lb. per 1000 cub. ft. and averages about 1 lb. In other words, approximately only 2 per cent. by weight of the gas is recovered as carbon.

Experiments are now being conducted in America with a view to the utilisation of the heat of combustion of the gas during the formation of carbon black, and the W. Sharpe[17] process, using hollow drums, claims to produce a considerable amount of power from the waste heat. If the experiments are successful, this would put the carbon black industry on an entirely different footing.

Full details of the manufacture of carbon black are given by R. O. Neal and G. St. J. Perrott[18] in a Bureau of Mines publication, which should be consulted by those interested in the subject.

R. T. Elworthy[19], in discussing the possibilities of manufacture of carbon black in Canada, states that there are four or five natural

[14] *Nat. Petr. News*, 1924, **16**, 18.
[15] *Ibid.*, 1923, **15**, 99.
[16] *U.S. Bureau Mines*, 1924.
[17] *Oil Trade J.*, 1924, **15**, 2, 76.
[18] *U.S. Bureau Mines Bull.* 192, 1922.
[19] *J. Inst. Petr. Techn.* **10**, 356, 1924

gas fields in Alberta where the establishment of the industry might be considered. The present British consumption is about 10,000,000 lb. annually and the Canadian imports 3,000,000 lb. These supplies come from the United States, and competition for the trade would be keen. Canada would be at a disadvantage because of high freight costs from the Northern Alberta fields.

Hard Carbon and Hydrogen.

By the thermal decomposition of natural gas there is produced hydrogen and a hard form of carbon suitable for the manufacture of electrodes, etc. The decomposition is carried out at approximately 1600° C. and the hydrogen obtained is practically pure. The investigations of Szarvasy[20] have resulted in the industrial exploitation of the dry Transylvanian gases for this purpose, and by a special process in which the carbon is deposited on a previously prepared carbon surface, it is claimed that a peculiarly pure and suitable electrode carbon is produced.

Helium.

Helium occurs in notable quantities in many natural gases. In Texas gases are known which contain 1–2 per cent. helium. According to J. C. McLennan[21] the gases within the British Empire which are richest in helium are those of Alberta and Ontario with about 0·3 per cent. The Heathfield, Sussex, gas contains 0·2 per cent., and that from Bath springs 0·15 per cent.

Helium is particularly suited for filling airship envelopes as it is non-inflammable and has a lifting power only 8 per cent. lower than that of hydrogen. It can be mixed with hydrogen to the extent of 15 per cent. without the mixture becoming combustible. In a report by R. B. Moore[22] an account is given of the plants erected in Texas for supplying helium to the air services of the U.S. Army and Navy. The gas used contained 0·95 per cent. helium. The method of operation is to liquefy all the components of the natural gas except the helium and part of the nitrogen, and in a second operation to remove the remaining nitrogen by liquefaction. The Linde cooling system has proved the most efficient. The plants are capable of producing 30,000 to 40,000 cub. ft. of helium daily.[23] In the large plant at Fort Worth helium can probably

[20] E.P. 159,823.
[21] *British Science Guild pamphlet*, 1923.
[22] *Bureau Mines Tech. Rept.* 2363, 1923.
[23] McLennan, *loc. cit.*

be produced at 10 cents per cubic foot, but it is believed that the cost will ultimately be reduced to 3 cents. This latter figure is also the ultimate estimated cost of the product from the plant now being built at Washington to provide 1,500,000 cub. ft. per day for the U.S. Navy.[24]

It is of interest to note that the Canadian Government is taking vigorous steps to conclude a thorough field survey for helium.[25]

Other Constituents of Natural Gas.

Although commercial processes are still not available for the manufacture of methyl alcohol and its derivatives from methane, much work continues to be done on the subject, and it is apparent that the problem approaches successful solution.

As regards direct partial oxidation of methane for the production of formaldehyde, the conditions governing the yield are those of catalysis, temperature control and efficient mixing. T. S. Wheeler and E. W. Blair[26] have proceeded with their investigations on the oxidation of hydrocarbons, and find that slow oxidation and a short time of heating are important factors in determining a high yield of formaldehyde from methane.

The greatest success in the manufacture of chemical compounds from natural gas has been attained by direct chlorination. The commercial preparation of methyl chloride is now being carried out successfully[27], and chloroform and carbon tetrachloride can also be made, though not yet sufficiently cheaply to compete with existing methods. Recently A. Schleede and C. Luckow[28] have published a detailed study of the direct chlorination of methane when the two gases are passed together through electrically heated quartz tubes.[29]

Investigation is now being concentrated on the replacement of the chlorine in methyl chloride by hydroxyl to form methyl alcohol. R. H. McKee and S. P. Burke[30] have gone deeply into the question and have published a detailed study of the mechanism of the reactions involved in the hydrolysis. They have obtained results with calcium hydroxide which give promise of commercial possibilities. At 350° C. the best yield obtained was 67 per cent. of methyl alcohol.

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[24] *Chem. Met. Eng.*, 1924, **31**.
[25] *Loc. cit.*
[26] *J. Soc. Chem. Ind.*, 1923, 81T.
[27] *Cf. Bureau Mines Tech. Paper* 255.
[28] *Ber.*, 1922, **55**, 3710.
[29] *Cf. J. Inst. Petr. Techn.* **10**, 622, 1924.
[30] *Ind. Eng. Chem.*, 1923, **15**, 682.

Special Uses of Natural Gas.

The U.S. Bureau of Mines has carried out large scale experiments on the use of highly volatile natural gasoline as a refinery refrigerant for cooling wax distillates. L. D. Wyant[31] gives a working description of the plant, which appears to offer considerable promise of providing a cheap and in many cases readily obtainable cooling medium in place of the usual ammonia or carbon dioxide. The only disadvantage is the risk of fire, which, however, should not be great. The use of highly volatile hydrocarbons for this purpose is not a novelty. According to J. Bryson and A. C. Thompson[32] this method was in use in the Scottish refineries over fifty years ago, and in 1881–4 was common practice in Scotland, spirit of sp. gr. 0·66 being successfully used.

In the Rivadavia field W. Friedmann[33] has attempted to utilise waste natural gas in place of steam for distillation purposes, and has also had successful results in treating strongly emulsified oils by its aid. These oils, containing 30 per cent. of water, are otherwise undistillable.

Though it is true that more and more attention is being paid to the utilisation of oil-field gas, there is in many fields an inordinate production of gas, and this leads inevitably to an unnecessarily rapid cessation of the flowing life of the fields and exhaustion of the petroleum-bearing strata. To the loss of pressure in the wells due to this cause J. Strijow[34] ascribes the diminished production or exhaustion of many of the Grozni strata, and the same thing applies in many other fields. It is obvious that steps will have to be taken to prevent the free escape of gas or to return it to the producing strata.[35]

In this connection a striking demonstration of the effect of extraneous gas introduced into an oil sand has been given in the Lyons-Quinn field of Oklahoma and is described by A. F. Hinton.[36] In this case the introduction of the gas was accidental and resulted from the migration of gas from a separate sand. The Bureau of Mines, through M. J. Kirwan[37], conducted a thorough investigation of the occurrence. It was estimated that 1444 million cub. ft. of gas entered the productive oil sand and that the production of oil had been increased by 950,000 barrels. It is believed that this oil would not have been recovered by ordinary methods. On

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[31] *Nat. Petr. News*, 1923, **15**, 99.
[32] Private Conversation, 1923.
[33] U.S. Pat. 1,456,570.
[34] *J. Inst. Petr. Techn.*, 1923, **9**, 272A.
[35] *Cf.* A. B. Thompson, *ibid.*, 1923, **9**, 314.
[36] *Nat. Petr. News*, 1924, **16**, 28.
[37] *U.S. Bureau Mines Bull. Serial* 2612, 1924.

the other hand, though the casing-head gas was largely increased, its gasoline content was not, and this caused loss and inconvenience to the natural gasoline operators. Even taking the high value of 10 cents per 1000 cub. ft. for the gas, and with oil at $2 per barrel, there was left a balance of nearly $1,400,000 in favour of using gas as a stimulant to oil production.

Notes on Cleaning of Tankers.

By H. BARRINGER, M.Inst.C.E., M.I.Mech.E.

THE question of the cleaning of tank vessels after carriage of various liquids is one of importance, especially under the Harbour Regulations lately brought into force, and it may therefore be of interest to briefly summarise the methods employed at the present time under various conditions.

Petrol.—This, of course, leaves no residue in tanks, but rust is rapidly formed on surface of plates, and should be removed from time to time by wire brushing and washing out. In order to render tanks safe to work in, it is necessary to introduce steam, which evaporates any drainings of petrol left, and expels the vapour, ventilation being supplied by windsail or ejectors. Before any work can be carried out it is necessary to obtain a chemist's certificate stating that tanks are free of gas. This test is made with the well-known Redwood apparatus.

Should there be any sediment in tanks it is advisable to remove same and wash out with water before steaming.

Kerosene.—In order to clean tanks it is usual to wash out with water, and afterwards to steam out and ventilate with windsails and ejectors. Deposit, if any, to be first removed.

Crude Oil.—After carrying crude oil it is usual to wash out with water, a hot water hose being the best if obtainable; afterwards tanks are steamed and ventilated with windsails and ejectors. It is necessary to take the same precautions with crude oil as with petrol.

Liquid Fuel.—Water washing is carried out together with steaming and ventilation; hot water, if procurable, is the best.

Molasses.—Tanks, after the carriage of Molasses, are easily cleaned by water, salt water being found the best for the purpose.

Whale Oil.—Washing and steaming is necessary.

The above methods are such when vessel is continuing to carry the same product and is necessary to remove sediment, etc.,

but if a vessel after carrying one of the heavier oils, fuel, crude, or whale, etc., is required to be cleaned for the carriage of a lighter oil, cleaning is a much more tedious and expensive operation. After some of the heavy oil has been removed by washing and steaming, it is necessary to wipe down and again wash and steam, and finally to wash out with kerosene, the dirty oil being returned to the shore. Probably one or more further steamings and washings will be required. It will, therefore, be realised that it is important to keep vessels carrying as far as possible one class of oil, as a vessel having once carried a heavy oil it is difficult and expensive to prepare for the carriage of a lighter oil, which might be discoloured or contaminated by placing in a tank not thoroughly clean. Caustic soda is often used to assist in removal of oil.

When vessel is in close waters, harbours, rivers, docks, etc., no contaminated water is allowed to be pumped overboard. In this case, unless vessel proceeds to sea specially for the purpose, it is necessary to discharge either through some oil extracting apparatus on board vessel, or ashore, or into barges specially fitted to purify the water before being discharged overboard.

Several purifiers are obtainable, all dependent in their action primarily on the difference in specific gravity of oil and water, combined with heating coils when dealing with heavy oils, and comprise apparatus which can be fixed on board or ashore or on barges alongside.

The Desulphurising of Crude Oil Distillates by Means of Hypochlorite, after the Method of Dunstan and Brooks.

By Prof. H. I. Waterman, Ph.D., and J. H. Heimel.[1]

By some simple experiments it was verified that the application of the method of Dunstan and Brooks[2] to certain distillates from Persian crude, of sp. gr.=0·830 with 0·5 per cent. sulphur and of sp. gr.=0·870 with 1·5 per cent. S., results in considerable sulphur reduction.

Later the effect of hypochlorite on a series of sulphur compounds was investigated, the compounds being contained in a Persian distillate of sp. gr.=0·780 to 0·800 which boiled between 150° and 230° C. For our purpose the amount of sulphur in this distillate (0·1 per cent.) could be neglected.[3] The following sulphur compounds were investigated:—$(C_6H_5)_2S$, $(C_6H_5)SH$, $(C_2H_5)_2S$, $C_2H_5.SH.C_6H_5.N.:C:S$, $C_6H_5.SCN$, CS_2, $(C_6H_5)_2SO_2$, $(C_6H_5)_2SO$, $(C_2H_5)_2SO_2$, C_4H_4S (thiophen), and $C_2H_5.SCN$. The sulphur compounds went into solution or could be divided into sufficiently fine particles by shaking. The diphenyl sulphone could not be held in suspension, and it was therefore dissolved in a small quantity of alcohol and this dissolved in the oil.

About 50 c.c. of the oil containing the particular sulphur compound was shaken for some hours with 250 c.c. of a 0·6 N solution of sodium hypochlorite. Oil was then worked several times with a solution of sodium carbonate and with water and was finally filtered by suction three times through a filter containing bauxite of approx. 2 cm. thickness. By this operation considerable decolorisation was obtained. The amount of sulphurin the refined oil was estimated by the method of Carius. Under these conditions it was shown that phenyl mercaptan, diethyl sulphide, phenyl mustard oil, phenyl thiocyanate, and diphenyl sulphoxide were substantially removed. Diphenyl sulphide ethyl mercaptan, carbon disulphide, diphenyl sulphone, diethyl sulphone and ethyl thiocyanate were completely removed.

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[1] Compare *Chem. Weekblad.*, 1924, **21**, 374. This is the same paper in somewhat more detailed form.

[2] A. E. Dunstan and B. T. Brooks. Refining of Gasoline and Kerosene by Hypochlorite, *J. Ind. Eng. Chem.*, 1922, **14**, 1112.

[3] Compare a sulphur content of 0·08 per cent. in an analogous distillate, sp. gr. = 0·785. A. E. Dunstan. The Crude Oil of Maidan-i-Naftun, *J. Inst. Petr. Techn.*, 1924, **10**, 57.

Compound of sulphur.	Sulphur percentage before refining (theoretical).	Percentage of sulphur after refining.
$(C_2H_5)_2S$	2·0	Practically free from sulphur.
C_2H_5SH	1·7	0·4
$(C_2H_5)_2S$	1·8	0·5
C_2H_5SH	1·8	Practically free from sulphur.
$C_2H_5N:C:S$	1·3	0·2
$C_6H_5S:CN$	1·3	0·5 (0·7, when not treated with bauxite)
	1·2	0·4
CS_2	1·4	Practically free from sulphur.
	2·1	Practically free from sulphur.
$(C_2H_5)_2SO_2$	0·3	Practically free from sulphur.
$(C_2H_5)_2SO$	1·3	0·4
$(C_2H_5)_2SO_2$	1·6	Practically free from sulphur.
C_4H_4S (thiophene)	1·2	1·0
$C_6H_5S:CN$	1·6	Practically free from sulphur.

The removal of carbon disulphide was very complete. To prevent loss of this low-boiling substance cooling was applied during treatment with the hypochlorite. Thiophen behaves differently, for only a small proportion was removed. In this connection it was noticed that Persian and Mexican distillates did not give the well-known blue colour (indophenin reaction) with isatin and concentrated sulphuric acid, so that these oils seem to contain no thiophen.

Dunstan[4] has shown that the treatment with hypochlorite, the initial and final alkali washes, the redistillation and the filtration through bauxite each have a definite desulphurising action. In an experiment with phenyl thiocyanate, it was noticed that without the bauxite filtration the sulphur content was 0·7 per cent., whereas after the bauxite filtration it was 0·5 and 0·4 per cent. respectively.

Experiments with Distillates of Mexican Oil.

The sulphur content was determined at each stage of the refining. The oil was first washed with 1 vol. of 10 per cent. caustic soda solution[5] for two hours. The concentration of hypochlorite in these experiments was 0·6N (Dunstan uses 0·2 to 0·3 N). The concentration of free alkali was approx. 0·5 gm. caustic soda per litre.[6] The first hypochlorite wash was of 1 vol. and the mixture was shaken for 1½ hours. The second hypochlorite wash was similar, but the concentration of free alkali was reduced to 0·2–0·3 gm. caustic soda per litre, and during the shaking carbon

[4] *J. Inst. Petr. Techn.*, 1924, **10**, 62, 65. *Chem. Weekblad.*, 1924, **21**, 193.
[5] A. E. Dunstan. The Crude Oil of Maidan-i-Naftun, *J. Inst. Petr. Techn.*, 1924, **10**, 61. In the present experiments a much greater alkali-wash was used than mentioned here.
[6] Method of estimation of free alkali was that of Blattner. *Lunge, Soda-industrie*, 1909, **3**, 505.

dioxide was introduced. In this way the stability of the hypochlorite was decreased, and, as Dunstan has also shown, considerable chlorination occurred. After the second hypochlorite treatment the oil was washed with caustic soda solution (104 gms. per litre) and then with water. Finally it was filtered through a layer of bauxite approx. 10 cm. thick. The bauxite had previously been roasted to 550° C. and was introduced into the filter while still warm. The amount of sulphur removed after each stage of the refining was determined. The bromine numbers, determined according to the method of McIlhinery, were small (4, and lower), which indicated the saturated character of the distillates. The following table gives the characteristics of two Mexican distillates and the reduction in sulphur content produced by each stage of the refining.

Sp.gr.	0·830–0·850	0·890–0·940
Sulphur content of original	1·28 per cent. S	2·95 per cent. S
Proportion of total sulphur removed by—		
1st soda wash	3 per cent.	7 per cent.
1st hypo wash	19 „	6 „
2nd hypo wash	6 „	2 „
2nd soda wash	14 „	12 „
Bauxite filtration	26 „	13 „
Complete refining process	68 „	40 „
Chlorine content—		
After 1st hypo. treatment	0 „	0 „
After 2nd hypo. treatment	1·1 „	1·1 „

It is shown that the method of Dunstan gives satisfactory results with Mexican distillates, no less than 68 per cent. of the sulphur being removed in the case of the lower-boiling distillate. The introduction of chlorine into the oil in the case of the second hypochlorite treatment was due to the acidity of the hypochlorite: if the free alkali content is kept sufficiently high, as in the first hypochlorite wash, then no chlorination results. It is important to keep the oil free from chlorine, because the presence of halogens in the oil can cause the formation of gum. In an experiment with a low-boiling distillate obtained by the cracking of gas-oil in retorts we found that the action of bromine, even when cooled in ice, caused the formation of bromine-containing products, which on distillation, at 100° C. even, gave rise to a deposit of "carbon."[7] This is in accordance with the classic research of T. E. Thorpe and J. Young,[8] who observed that the action of bromine on cracked distillates produced a dark, tany substance in the bottoms of

[7] Experiment by J. N. J. Perquin and L. W. H. Borgesius.
[8] *Ann.*, 1873, **165**, 14.

their vessels. F. J. Nellensteyn has also obtained "carbon," which persistently holds iodine, by the action of iodine as unsaturated hydrocarbons.[9]

From the behaviour of the different sulphur compounds and of the Mexican distillates we can confirm Dunstan's opinion, his method being satisfactorily applicable to light distillates from various sulphur-containing oils.

We wish to thank Mr. J. N. J. Perquin, who was good enough to make some check determinations.

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[9] F. J. Nellensteyn. *Chem. Weekblad.*, 1924, **21**, 102. Not only halogens but also particular sulphur compounds can in some circumstances give rise to gum. Compare The Refining and Recovery of Petroleum Products with Silica-Gel, Bulletin No. 4, Silica-Gel Corporation, Baltimore, 1924.

The Estimation of Lead Tetraethyl in Motor Spirit.

By Stanley Francis Birch, Ph.D.

In view of the importance of lead tetraethyl, due to its recent use in motor spirits as an "anti-knocking" body, it appeared desirable that some method of estimating this substance should be devised. It has been found that the method to be described gives sufficiently accurate and trustworthy results for most purposes.

Lead is most conveniently estimated in the form of its sulphate. It is therefore fortunate that the action of concentrated sulphuric acid on lead tetraethyl rapidly and quantitatively converts it into lead sulphate. Moreover, after removing the lighter spirit by evaporation, if a little potassium nitrate is added, the continued action of the same reagent at a higher temperature completely destroys all the organic matter. On dilution, the lead can then be estimated in the usual manner.

For the concentrations of lead tetraethyl which are reported to be used in commercial motor spirits, the following experimental procedure has been adopted :—

Fifty c.c. of the spirit are placed in a 200 c.c. Kjeldahl flask and 15 c.c. of concentrated sulphuric acid added. After shaking, the flask is allowed to stand for half-an-hour and the light spirit then driven off through a condenser by means of a small flame. The rate at which the spirit is removed can be considerably increased by an occasional shaking of the flask. When no more spirit distils over, the condenser is removed, and, after another 20 c.c. of concentrated sulphuric acid have been added, the mixture heated for half-an-hour in the manner usually adpoted for Kjeldahl determinations. It is then allowed to cool considerably, 7-10 gms. of potassium nitrate (in large crystals) added and the heating continued over a small flame until no more brown fumes are evolved. The liquid in the flask should then be pale yellow in colour. (It may be necessary to add a further quantity of potassium nitrate and repeat this process.) When cold, the contents of the flask are diluted with water and transferred to a 500 c.c. beaker; the total volume of the solution should be approximately 300 c.c. It is boiled for a short time to coagulate the precipitate and, after standing overnight, filtered through a Gooch crucible the next day. The precipitated lead sulphate is washed with 10 per cent. sulphuric acid and alcohol in the usual way and dried to constant weight at 110°.

The accuracy of the method was tested on a solution prepared by dissolving a weighed quantity of lead tetraethyl in a given volume of spirit. This solution should theoretically have contained 0·161 per cent. of lead tetraethyl; the figures actually found were 0·157 per cent. and 0·154 per cent. Taking the lower of these, the error is 0·007 per cent. When it is considered, however, that lead tetraethyl decomposes in the presence of air, and that such decomposition must certainly have occurred during the weighing of the lead tetraethyl, it will be realised that the figure 0·161 per cent. is only a maximum possible figure and that the percentage error of the method is therefore considerably less than 4 per cent. There can be, of course, no possibility of obtaining too high a result.

These estimations have now been carried out over a period of six months, and it is interesting to note the stability of lead tetraethyl in spirit which is shown by the following figures. A solution of lead tetraethyl in spirit (S.G. 726/60°), which gave on analysis the figures 0·164 and 0·170 per cent., was kept in a metal can out of contact with light and air. After seven days and six months respectively, the figures obtained were 0·162 per cent. and 0·167 per cent. Another sample, found to contain 0·305 per cent. of lead tetraethyl became cloudy on exposure to light, even in the absence of air, and deposited a yellowish-white flocculent precipitate. However, even after seven days' exposure the percentage of lead tetraethyl determined on a filtered sample was 0·282 per cent., or a loss of a little over 5 per cent. of the total lead tetraethyl present. From these results it would appear that, providing precautions are taken to exclude light and air, no deterioration need be feared during storage.

My thanks are due to the Anglo-Persian Oil Co., Ltd., for permission to publish these results.

Geophysical Surveys as Aids to the Geologist.

By E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S.

Of recent years much attention has been given by physicists to the perfecting of instruments to record minute differences in gravity and other physical quantities. The Torsion Balance has, perhaps, attracted most interest and has given the most striking results.

By its use minute differences in gravity values can be determined, and when a number of results are plotted a map showing isogams or lines of equal intensity encircling areas of low or high gravity is obtained.

This method has been used extensively in connection with petroleum work in the plains of Hungary and other countries, especially where the presence of salt domes is suspected, the low specific gravity of the salt masses giving very definite results, and thus areas of low gravity can be mapped out.

Where domes of older and heavier rocks are indicated, areas of high gravity can be delineated, and this is especially noticeable when a solid limestone is overlaid by ordinary sand and clay sediments.

The results have been in some cases so definite that drilling is being undertaken to test the underground structures that are indicated. There is at least one authenticated case of an oilfield (the Egbell field) being discovered by this method.

It is only in flat country that the Torsion Balance can be employed with confidence: hilly ground, or the presence of hills in the near neighbourhood, cause so many complications that it is difficult to determine the normal local value of gravity the divergences from which, either above or below, give the indications of concealed structure when plotted carefully and methodically on a map.

It will be noted also that it is at the best only geological structures that can be indicated; it does not follow that petroleum will be associated with any favourable structure that may be discovered.

In the coastal plain areas of Texas, Louisiana and Arkansas, that is to say, the low-lying land that extends right up to the Palæozoic outcrop, the oil and gas fields are probably all associated with salt domes, though in many cases these may be in an incipient stage and very deeply buried. It is true that in many of the proved fields no signs of an intrusive salt mass have been detected,

but the general orientation of the fields and the distinct but very gentle structures that have been revealed by extensive drilling, point to the probability of salt-dome action. The minor faulting that has occasionally been proved is also quite consistent with the salt-dome theory. Therefore, the discovery of an enclosed "minus" area *i.e.*, where the isogams—the gravity contours so to speak—are disposed in concentric rings about a locality where the gravity value is below the normal, must be considered a very important step towards the finding of a new oil or gas field.

In countries or states where geological evidence at the surface is so scanty as to be almost negligible, the geologist must make use of every means to obtain information as to concealed structures, and the Torsion Balance, used in connection with a geological survey, may enable astonishing results to be achieved.

There is happily another method that may be employed to confirm or supplement the evidence obtained from a Torsion Balance survey. It is well known that around some of the greatest oilfields there is a disturbance of the earth's magnetic field, both the directions and the spacing of the lines of equal magnetic variation are affected, and probably the declination.

The writer pointed out some years ago that a mass of oil-impregnated rock surrounded by similar strata impregnated with water might be detected by plotting the density of the magnetic field, noting especially the vertical component. An oil-bearing area must necessarily be a poorer conductor than a water-bearing area, and thus the density of the magnetic field should decrease over an oilfield, and a careful magnetic survey made with very delicate instruments may give very clear indications of the presence of petroleum in quantity.

This method has actually been used in the last two or three years in certain European countries and has given remarkable results by plotting magnetic contours, closed minus and plus areas being delineated. The significance of such evidence has not yet been proved by experimental drilling on an extensive scale, but there is no reason to doubt the accuracy of the observations made.

Here, then, are two methods which can be employed in conjunction in land where surface evidence is at a minimum, the one to detect hidden structures and the other to detect concealed stores of petroleum. In cases where both indicate a definite locality, there is a prima facie case for an experimental well.

The plains of Hungary, Rumania, the South-Western states of the U.S.A., and many other countries afford ideal areas in which these methods can be tested, and without making any extravagant claims for either method we may be sure that interesting and possibly very important results will be obtained. The scientific

geologist certainly cannot afford to disregard the help that geophysical surveys can give him when confronted with unreadable ground.

There have been many oil-finding instruments designed, and often extensively advertised in the past; all that the writer has personally seen are of the "doodlebug" type, more calculated to extract dollars from the pockets of the credulous than to fill them by pointing to where oil can be struck. But the methods briefly described above are founded on well-known and understood phenomena, and have been elaborated and perfected by men of high position in the scientific world. There can be no doubt that there is a future for geophysical surveys to supplement the work of the geologist in countries where surface evidence fails. In this connection a Hungarian scientist, Professor Rybar, is already undertaking the training of experts in the use of the Torsion Balance and other instruments, in order that they may be able to undertake expeditions to different countries, where, under the guidance of local geologists, they may make geophysical surveys. By such co-operation it is hoped that much that is now hidden in Nature's bosom may be revealed for the benefit of the practical exploiter of oilfields.

Conversion of Petroleum Weights and Measures.

By George Sell.

Whilst the units of weight and volume used for petroleum remain so varied, and the possibility of the adoption of one standard weight and one standard measurement seems so remote, a few remarks on the conversion of weights to measures and *vice versa*, and the consideration of a quick and yet reliable method of carrying out such conversions appear to be warranted.

The various units of weight now in common use are the ton of 2240 lbs. av., the short ton of 2000 lbs. av., the metric ton of 1000 kilograms or 2204·6223 lbs. av., and the pood of 36·1127 lbs. av., while the units of volume are the imperial gallon of 277·274 cub. ins., the U.S.A. gallon of 231 cub. ins., the barrel of 35 imperial, or 42 U.S.A. gallons, the litre, the cubic centimetre, the cubic metre, and the koku.

The conversion of weights from one unit to another, and of volumes from one unit to another, is a simple operation. It involves only the use of the factor for the ratio of such units and can be carried out by direct multiplication or from conversion tables. A useful list of these factors and a number of tables of equivalents are to be found in Redwood and Eastlake's "Petroleum Technologist's Pocket Book,"* from which the following have been extracted :—

To convert	Multiply by	Reciprocal.
Tons av. to Kilograms	1016·0475	0·000984
Tons av. to Metric Tons	1·016	0·9842
Tons av. to Poods	62·02804	0·01612
Tons av. to Short Tons	1·12	0·8929
Short Tons to Kilograms	907·1858	0·001102
Short Tons to Metric Tons	0·9072	1·1023
Short Tons to Poods	55·38218	0·01805
Metric Tons to Poods	61·04839	0·01638
Imperial Gallons to Cubic Centimetres ..	4543·457	0·00022
Imperial Gallons to U.S.A. Gallons ..	1·2	0·833
Imperial Gallons to Koku	0·02519	39·7
Imperial Gallons to Litres	4·543457	0·22009
U.S.A. Gallons to Cubic Centimetres ..	3784·69968	0·000264
U.S.A. Gallons to Koku	0·021	47·618
U.S.A. Gallons to Litres	3·784699	0·26422

The converting of weights to volumes, and of volumes to weights, however, presents a more difficult problem as it is necessary to

* 2nd Ed. revised by Arthur W. Eastlake. Charles Griffin and Co., London, 1923.

take into consideration the specific gravity of the oil and, in some cases, the coefficient of expansion. Where the specific gravity has been determined at a temperature other than that at which the volume measurement is made, a correction must be made for the coefficient of expansion. It is advisable that all measurements and gravities be taken at the standard temperature of 60° F. (15·5° C.), and gravities determined at other temperatures corrected by the use of the coefficients as laid down by the Standardization Committee of the Institution of Petroleum Technologists.†

To carry out weight and volume conversions by mathematical means is often a lengthy operation, and when such calculations are of frequent occurrence they tend to become tedious and monotonous, as will be seen from the following examples :—

1. To find the weight in Tons of 5000 Imperial Gallons of oil, sp. gr. 0·810:
$$\frac{5000 \times 10 \times 0{\cdot}810}{2240} = 18{\cdot}08 \text{ Tons} = 18 \text{ Tons } 3 \text{ Qtrs. } 17{\cdot}2 \text{ Lbs.}$$
2. To find the volume in Barrels of 250 Metric Tons of oil, sp. gr. 0·890:
$$\frac{250 \times 2204{\cdot}6223}{0{\cdot}890 \times 10 \times 35} = 1769{\cdot}36 \text{ Barrels.}$$
3. To find the volume in U.S.A. Gallons of 375 Tons of oil, sp. gr. 0·840:
$$\frac{375 \times 2240}{8{\cdot}33 \times 0{\cdot}840} = 120{,}048 \text{ U.S.A. Gallons.}$$

A series of tables to include every such possible calculation would be too cumbersome, and the working out of each calculation as and when required, unless infinitely accurate results are necessary, can be obviated by the use of the quick method dealt with here. This is carried out by means of charts, known as alignment charts, a small scale example of which is given in Figure 1. Three scales are used, one for volume, one for specific gravity, and one for weight. By the use of such charts the conversion of weights and measures resolves itself into the simple operation of carrying a line through the known factors on two of the scales and reading the result at the point of intersection on the third scale. This can be more conveniently done by the use of a straight-edge so that the chart is kept free from any pencil or ink lines. The use of decimals on the volume and weight scales is recommended as allowing any multiplication of the unit to be used by the alteration of the position of the decimal point. The three examples quoted above are marked on the illustration by the dotted lines, and it will be seen that the results obtained by this method closely approximate those obtained by mathematics :—

1. 18·10 tons.
2. 1770 barrels.
3. 120,000 U.S.A. gallons.

(†) Standard Methods of Testing Petroleum and its Products. The Institution of Petroleum Technologists, London, 1924.

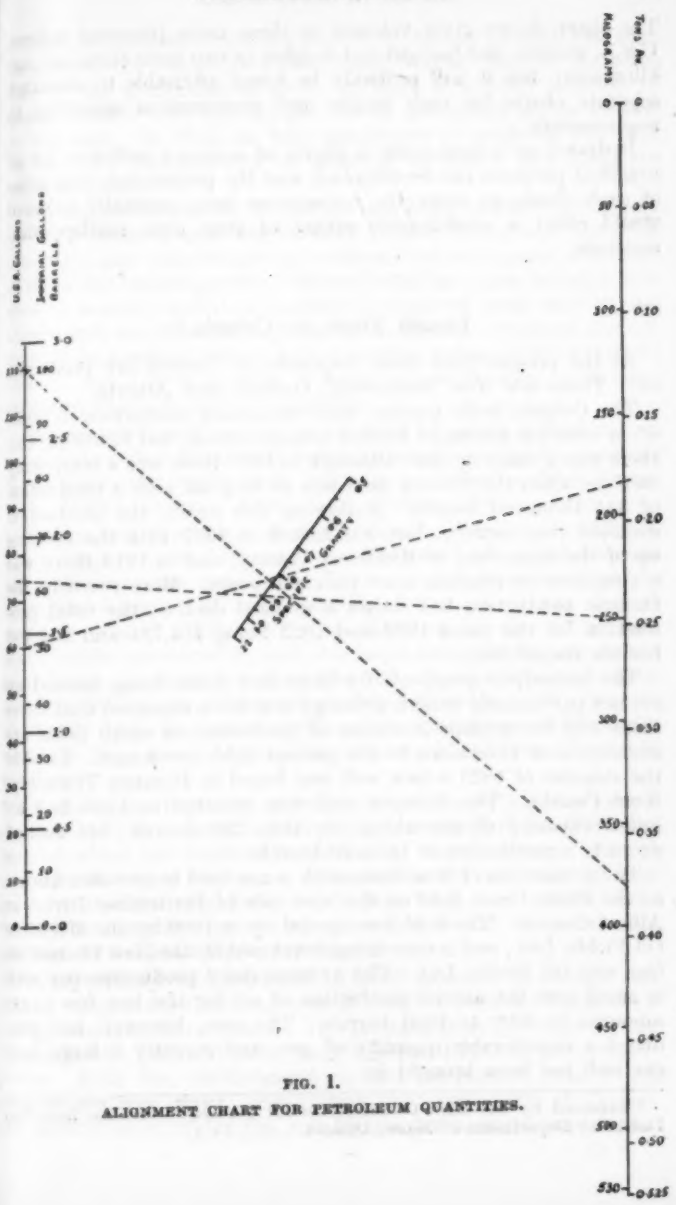

FIG. 1.

ALIGNMENT CHART FOR PETROLEUM QUANTITIES.

The chart shown gives volumes in three units (imperial gallons, U.S.A. gallons, and barrels) and weights in two units (tons av. and kilograms), but it will probably be found advisable to construct separate charts for each weight and measurement according to requirements.

If drawn on a large scale, a degree of accuracy sufficient for all practical purposes can be obtained, and the preparation of a series of such charts to cover the conversions most generally required would effect a considerable saving of time over mathematical methods.

Liquid Fuels in Canada.*

At the present time three Provinces in Canada are producing oil. These are New Brunswick, Ontario and Alberta.

The Ontario fields reached their maximum production in 1900, when over 900 thousand barrels were produced; but following this there was a sharp decline, although in 1907 there was a temporary increase when the Tilbury field was at its peak with a production of 344 thousand barrels. Following this again, the production declined very rapidly, but was halted in 1917 with the opening up of the Mosa field of Middlesex County, and in 1918 there was a considerable increase over previous years. More recently the Ontario production has shown a gradual decline, the total production for the years 1922 and 1923 being 164,731 and 159,400 barrels respectively.

The immediate prospects for large new fields being opened up are not particularly bright, although it is to be expected that there there will be sporadic increases of production as small fields are discovered or extensions to the present fields are found. Late in the summer of 1923 a new well was found in Romney Township, Kent County. The Romney well was reported to have had an initial capacity of something less than 200 barrels, but settled down to a production of 15 to 20 barrels.

The production of New Brunswick is confined to one area known as the Stony Creek field on the west side of Petitcodiac River, in Albert County. The field was opened up in 1909 by the Maritime Oil Fields, Ltd., and is now being developed by the New Brunswick Gas and Oil Fields, Ltd. The average daily production per well is small and the annual production of oil for the last few years amounts to 8000 to 9000 barrels. The area, however, has produced a considerable quantity of gas, and recently a large new gas well has been brought in.

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* Received by the High Commissioner for Canada in London from the Dominion Department of Mines, Ottawa.

In Alberta commercial production up to the present has been confined to the Sheep Creek field, south-west of Calgary. In addition to the production of crude oil there is a small recovery of gasoline made from natural gas in two absorption plants located in this area. In 1923 the total production of crude oil was 1943 barrels and the quantity of gasoline recovered was 1,342,114 imperial gallons.

Drilling operations for oil and gas are being carried on in many parts of Alberta, and late in 1923 British Petroleums Ltd. discovered a well near Wainwright with an initial capacity estimated at 60 to 100 barrels per day. Several wells are being drilled in this area at present, and it is confidently expected some encouraging results will be obtained. In the same area the Imperial Oil Co. brought in a well at Fabyan with a gas flow estimated at 14,000,000 cub. ft. and a good showing of heavy oil, while other wells have encountered gas in smaller quantities.

Revised statistics on the production of crude petroleum in Canada show that the average value per barrel received by operators in the producing provinces in 1923 was as follows:—New Brunswick, $4·04; Ontario, $3·00; and Alberta, $4·23.

Besides the producing oil fields Canada possesses in Alberta a very large deposit of bituminous sands which outcrop at frequent intervals along the Athabaska River and tributaries through an aggregate distance of approximately 200 miles in the district centring around McMurray. The thickness of the bituminous sands varies considerably over this large area, but the maximum is probably not much less than 200 feet. By laboratory methods the bitumen has on distillation produced as much as 69 per cent. of oil, but up to the present, although various prospects are under way, no large scale commercial process of extraction is being applied.

Oil shales are found in many parts of Canada, but the known deposits that have been worked or are considered of possible commercial value are confined to Manitoba, Saskatchewan, Ontario and the Maritime Provinces. The amount of oil shale of high grade in the Maritime Provinces is very large, and with a satisfactory commercial process of extraction would be a valuable addition to Canada's liquid fuel resources.

Another liquid fuel produced in small quantity is benzol and related compounds recovered as a by-product from the by-product coking ovens in Nova Scotia. The production in the years ending September 30, 1921 and 1922, was 292,452 and 246,541 gals. respectively. With the establishment of more by-product coke ovens such as are now under consideration in various parts of Canada the production of motor fuel will become increasingly important.

Discussion on "The Modern Rotary Drilling System."

By L. R. McCollum.*

The following communicated discussion has been received from Mr. H. Pennington, to which Mr. McCollum has not yet had an opportunity of replying:—

With reference to the coring of wells by the rotary system, Mr. McCollum does not seem to be informed as to the development of this, and since some of your members still look with suspicion upon this system, perhaps they would be interested in the art as practised in Texas, compared with California.

It is conceded that for geological and palæontological purposes a continuous core is necessary to secure a complete column for determining the thickness of the various strata from which subsurface structure may be outlined. While this has been done with the diamond drill, in hard formations, the rotary is the only system that has ever made a well upon the Gulf Coastal Plain because of the loose formations encountered, and since we always look for oil in sedimentary rocks, and not in igneous, the predominant class of drilling necessary for oil prospecting is through the softer formations.

The method of coring in California is to drill a small hole ahead of the large hole, or below, and when the formation changes, as indicated by the bit, the bit is removed and the core barrel run back into the hole to take the core. The barrel is then removed to get the core, and a full diameter bit run to ream the hole out to full diameter down to the depth penetrated by the core barrel. The full diameter bit is then withdrawn and a small bit run to "rat-hole" ahead to another break, when the operation is repeated.

Thus, it will be noted that this practice requires three round trips, out of the hole and back, of the drill-pipe per core. At a depth of 3000 feet the time per core averages 24 hours, and, since the cost of running a drilling rig in the United States is approximately $225·00 per day, the cost per core is $225·00. In Texas the average driller can take cores perfectly, but in California there are core-drilling companies who take the cores with the owner's rig, making a charge therefor of $150·00 to $250·00, so that cores in that State cost from $375·00 to $475·00 each.

It is obvious, then, that continuous cores are not taken with that method because of the expense.

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Our best method, just perfected in Texas, is to take a continuous core with a specially-designed barrel and bit. The core is withdrawn with the barrel by running the sand line down through the drill-pipe, catching the barrel and withdrawing it through the drill-pipe without removal of the drill-pipe. The writer has taken a core from a depth of 2640 feet in twenty-one minutes' time, and another in twenty-one minutes more and so on, with an average length of 9 feet each, so that this method of coring makes it possible to take a continuous core at a cost that is commercial.

This method will be used in the Tampico District shortly, the cores to be sent for analytical study, from which it is hoped to define sub-surface structure.

The rigs used for this work are also a new development; multi-cylinder motor driven using gasoline for fuel. The writer now has three rigs of this type, and the cost of continuous coring is approximately $1·25 per foot—all expenses, including transportation, erection, fuel, water, pay roll, bits and repairs to equipment.

One prospect hole just finished to a depth of 3300 feet cost $4124·80; the diameter is the same as made with a large steam rig.

The rotary is operated at high speed—200 to 300 R.P.M—and a diamond shoe may be run, should an extremely hard rock be encountered. The entire rig is of steel construction, including the derrick, making the weight low, as well as the cost.

Mr. McCollum uses data freely from other sources than his own research work: I find that in his paper he has taken verbatim from a paper written by me, "Mud Pumps Play Big Part in Making Hole," which appeared in "The Oil Weekly," Houston, October 13, 1923. The data in this paper of mine were secured from actual drilling practice, and although Mr. McCollum says that California drilling is more highly developed than anywhere in the world, we feel complimented that he selects material from drilling done in Texas to bear his assertion out, although I do think that he should have given the source of his information, especially when addressing an Association such as yours.

REVIEWS.

THE BLACK GOLCONDA: THE ROMANCE OF PETROLEUM. Isaac F. Marcosson. Pp. 369, 10 illustrations. Harper Bros., New York and London, 1924. 15s. net.

This work, which is dedicated to "The Wildcatter. Whose faith and Courage made the American Oil Empire possible," presents in non-technical language a record of the outstanding features in the history of the Petroleum Industry, together with intimate details of the international struggle for the possession of the world's oilfields.

In the first four chapters the Author discourses mainly on the endeavours of the British and United States Governments to obtain oil supremacy, and in Chapter I. arguments are advanced chiefly against what the Author terms the "closed door" policy of Great Britain, particularly with regard to Persia and Mesopotamia. Chapters II. and III. deal respectively with the histories of the Anglo-Persian Oil Company and the Royal Dutch-Shell Combine, while Chapter IV. details American operations to obtain oil in foreign countries.

Chapter V., the subject chapter of the book, gives an interesting record of the rise and fall of various American fields, and the three subsequent chapters refer in detail to California, Oklahoma and Texas, while Chapter IX. contains a history of the evolution of the Standard Oil Company.

Under the heading of "Oil in the Great War," Chapter X. deals with the use of petroleum during the war and with the means by which continuity of supplies was ensured.

Fake companies and the methods adopted by their promoters to obtain money from the public provide interesting reading in Chapter XI., and in dealing with the future of petroleum in the final chapter estimates of the future production of petroleum in the United States are discussed, together with the question of conservation and how and where future supplies are to be obtained.

Throughout the book a large number of references are made to the pioneers of the Petroleum Industry, and in a number of cases brief notes of their careers are given. Among others we note interesting records of the work of Viscount Cowdray, Lord Strathcona, Lord Bearsted, Sir J. Cadman, Sir H. W. Deterding, and Mr. W. K. D'Arcy.

The book is written in a fascinating manner and should provide interesting reading to those connected with the Petroleum Industry. G. S.

We have received from the United States Bureau of Standards the following publications:—

PUBLICATION No. 55, which contains a report of the proceedings of the Sixteenth Annual Conference of representatives from various States. Of interest to petroleum technologists are papers by H. R. Ester, on Temperature as a Factor in the Measurement of Gasoline, and by F. S. Holbrook, on Specifications and Tolerances for Vehicle Tanks.

BULLETIN No. 88. Specification for Asphalt for Unsurfaced Built-up Roofing. The specification discusses grading requirements, inspection, sampling and laboratory testing of the raw material. The procedure to be adopted for the determination of melting-point, penetration, ductility, volatility and solubility is laid down in full detail. A. E. D.